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INSTRUCTIONS TO ABSTRACTORS,

GIVING THE

NOMENCLATURE AND SYSTEM OF NOTATION

ADOPTED IN THE ABSTRACTS.

1. Before beginning to write an abstract, it is desirable to read through the whole of the original paper, in order to form a judgment as to its importance, and as to the scale on which the abstract should accordingly be made.

2. The abstract should mainly consist of the expression, in the abstractor's own words, of the substance of the paper.

3. The abstract should be made as concise as possible, consistently with a clear and accurate statement of the author's results or theories, due regard being paid to their import.

4. If an abstract of a paper on the same subject, either by the author of the paper abstracted, or by some other author, has already appeared, note should as a rule be made of this fact. Important references to the researches of others quoted by an author should be reproduced in the abstract. Always employ figures instead of Roman numerals for references, thus :— *Annalen,* **221**, 92, instead of ccxxi, 92.

5. If an abstractor is acquainted with papers previously published by other authors containing statements either practically identical with, or opposed to, those in the paper abstracted, and to which no reference is made, he should notice their agreement or contradiction in a foot-note.

6. As a rule, details of methods of preparation or analysis, or, generally speaking, of work, may be omitted, unless such details are essential to the understanding of the results, or have some independent value.

Nomenclature.

7. Employ names such as *sodium chloride, potassium sulphate, ethyl acetate,* and use the terminals *ous* and *ic* only in distinguishing compounds of different orders derived from the same elementary radicle ; such, for instance, as mercurous and mercuric chloride, sulphurous and sulphuric acid.

8. Term compounds of metallic and alcoholic radicles with the group

OH, *hydroxides* and not hydrates ; for example, potassium hydroxide, phenyl hydroxide, the name hydrate being reserved for compounds supposed to contain water of combination or crystallisation. Compounds such as CH_3ONa, C_2H_5ONa, $C_7H_{15}ONa$, &c., should be termed sodium methoxide, ethoxide, heptyloxide, &c.

9. Apply the term *acid* only to compounds of hydrogen with negative radicles, such as HNO_3, H_2SO_4, H_3PO_4, and denote the oxides which form acids by names such as sulphuric anhydride, carbonic anhydride. Term salts containing an amount of metal equivalent to the displaceable hydrogen of the acid, *normal* and not neutral salts, and assign names such as hydrogen sodium sulphate, hydrogen disodium phosphate, &c., to the acid salts. Basic salts are as a rule best designated merely by their *formulæ*.

10. Use names such as *methane*, *ethane*, &c., for the normal paraffins or hydrocarbons of the C_nH_{2n+2} series of the form $CH_3{\cdot}[CH_2]_5{\cdot}CH_3$, &c. The isomeric hydrocarbons are usually most conveniently represented by names indicating their relation to methane ; for example, $CH_3{\cdot}CH_2{\cdot}CH_2{\cdot}CH_3$ = propylmethane ; $CH_3{\cdot}CH(CH_3)_2$ = isopropylmethane or trimethylmethane ; or, although less frequently, by names such as di-isopropyl.

11. Term the hydrocarbons C_2H_4 and C_2H_2 *ethylene* and *acetylene* respectively (not ethene and ethine). Distinguish the homologues of ethylene, whenever possible, by names indicating their relation to it, such as methylethylene, dimethylethylene, &c., denoting the di-derivatives of the form $C_nH_{2n+1}{\cdot}CH{:}CH{\cdot}C_nH_{2n+1}$ as α-, and those of the form $CH_2{:}C(C_nH_{2n+1})_2$ as β-compounds, thus : $CH_3{\cdot}CH{:}CH{\cdot}CH_3$ = α-dimethylethylene ; $CH_2{:}C(CH_3)_2$ = β-dimethylethylene. Similarly, use names such as methylacetylene and dimethylacetylene for the homologues of acetylene of the form $CH{\vdots}C{\cdot}C_nH_{2n+1}$ and $C_nH_{2n+1}{\cdot}C{\vdots}C{\cdot}C_nH_{2n+1}$. Adopt the name *allene* for the hydrocarbon $CH_2{:}C{:}CH_2$, and indicate the relation which its homologues bear to it in the same manner as pointed out for acetylene.

12. Distinguish all alcohols, that is, hydroxyl-derivatives of hydrocarbons, by names ending in *ol* ; such as quinol, catechol, resorcinol saligenol, glycerol, erythrol, mannitol, instead of hydroquinone, pyrocatechin, resorcin, saligenin, glycerin, erythrite, mannite. Compounds which are not alcohols, but which are at present distinguished by, names ending in *ol*, may be represented by names ending in *ole*, if a systematic name cannot be given. For example, write indole instead of indol ; furfuraldehyde instead of furfurol ; fucusaldehyde instead of fucusol. Ethers derived from phenols, such as $C_6H_5{\cdot}OCH_3$, &c., hitherto called anisol, anethol, &c., may be distinguished by names ending in *oil*, as anisoil and anethoil.

Alcohols should be spoken of as mono-, di-, tri-, or n-*hydric*, according to the number of OH groups.

13. Compounds analogous to the acids of the lactic series containing the group OH should be termed *hydroxy*-derivatives, and not oxy-derivatives ; for example, hydroxyacetic and not oxyacetic acid. Compounds containing the analogous groups C_2H_5O, C_6H_5O, $CH_3{\cdot}COO$, &c., should in like manner be termed ethoxy-, phenoxy-, acetoxy-derivatives. Thus

ethoxypropionic acid instead of ethyl-lactic acid; 3 : 4 diethoxybenzoic acid instead of diethylprotocatechuic acid; and acetoxypropionic acid instead of acetyl-lactic acid. Terms such as diethylprotocatechuic acid should be understood to mean a compound formed by the displacement of hydrogen-atoms in the hydrocarbon radicle of protocatechuic acid by ethyl, viz., $C_6H(C_2H_5)_2(OH)_2\cdot COOH$, and not $C_6H_3(OC_2H_5)_2\cdot COOH$, just as dibromoprotocatechuic acid is understood to be the name of a compound of the formula $C_6HBr_2(OH)_2\cdot COOH$.

14. The term *ether* should be restricted to the oxides of hydrocarbon radicles, and the so-called compound ethers should be represented by names similar to those given to the analogously constituted metallic salts (comp. 12).

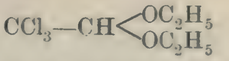
15. Compounds of the radicle SO_3H should, whenever possible, be termed *sulphonic* acids, or failing this, *sulpho-compounds*: as benzenesulphonic acid, sulphobenzoic acid, and not sulfi-compounds. Compounds of the radicle $SO_2\cdot NH_2$ should be termed sulphonamides.

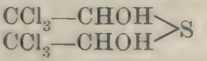
16. Basic substances should invariably be indicated by names ending in *ine*, as aniline, instead of anilin, the termination *in* being restricted to certain neutral compounds, viz., glycerides, glucosides, bitter principles, and proteids, such as palmitin, amygdalin, albumin. The compounds of basic substances with hydrogen chloride, bromide, or iodide should always receive names ending in *ide* and not *ate*, as morphine hydrochloride and not morphine hydrochlorate.

Notation.

17. Equations should *be omitted* unless essential to the understanding of the results; they, as a rule, should *not* be written on a separate line, but should "run on" with the text.

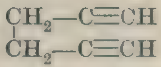
18. To economise space, it is desirable: 1, that *dots* should be used *instead of dashes* in connecting contiguous symbols or radicles, whenever this does not interfere with the clearness of the formula; 2, that formulæ should be shortened by the judicious employment of the symbols Me for CH_3, Et for C_2H_5, Pr^{α} for $CH_2\cdot CH_2\cdot CH_3$, Pr^{β} for $CH(CH_3)_2$, Ph for C_6H_5, Ac for $CO\cdot CH_3$, and Bz for $CO\cdot C_6H_5$; and 3, that formulæ should be written *in one line* whenever this can be done without obscuring their meaning. For example:

$CCl_3\cdot CH(OEt)_2$ instead of  $CCl_3{-}CH{<}\begin{matrix}OC_2H_5\\OC_2H_5\end{matrix}$

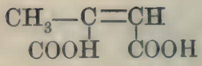
$[CCl_3\cdot CH(OH)]_2S$ instead of  $\begin{matrix}CCl_3{-}CHOH\\CCl_3{-}CHOH\end{matrix}{>}S$

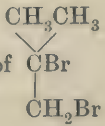
$CH_2{:}CH_2$ instead of $CH_2{=}CH_2$

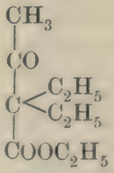
$CH\vdots CH$ instead of $CH{\equiv}CH$

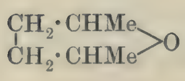
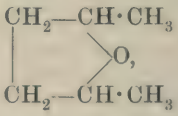
$CH\vdots C\cdot CH_2\cdot CH_2\cdot C\vdots CH$ instead of  $\begin{matrix}CH_2{-}C{\equiv}CH\\|\\CH_2{-}C{\equiv}CH\end{matrix}$

$CHMe{:}CHPr^{\alpha}$ instead of $CH_3\cdot CH{=}CH\cdot CH_2\cdot CH_2\cdot CH_3$,

$COOH\cdot CH:CHMe\cdot COOH$ instead of 
$CH_3-\underset{COOH}{C}=\underset{COOH}{CH}$

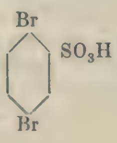
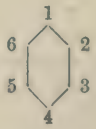
$CH_2Br\cdot CBrMe_2$ instead of 

$CEt_2Ac\cdot COOEt$ instead of 

 instead of 

$CHPh(OBz)\cdot CH(OBz)\cdot COOEt$ instead of
$C_6H_5\cdot CH(O\cdot CO\cdot C_6H_5)\cdot CH(O\cdot CO\cdot C_6H_5)\cdot COOC_2H_5$.

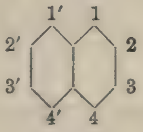
19. In representing the constitution of benzene derivatives, as a rule, merely indicate the relative positions of the radicles in the symbol of benzene by figures, instead of by means of the hexagon symbol, for example :—

Paradibromobenzenesulphonic acid, $C_6H_3Br_2\cdot SO_3H$ [Br : SO_3H : Br = 1 : 2 : 4] instead of  the figures always being used in the order 

Relatively to the position 1, the positions 2 and 6 should always be spoken of as *ortho*-positions, 3 and 5 as *meta*-positions, and 4 as the *para*-position. It is better, however, in speaking of the derivatives of benzene, to express their constitution by giving them names such as 1 : 2 dibromobenzene, 1 : 3 dibromobenzene, &c., rather than by terming them ortho- or meta-dibromobenzene, &c.

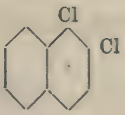
20. Moreover, in representing the constitution of derivatives of other "closed chain" hydrocarbons, do not, as a rule, employ graphic formulæ, but merely indicate the position of the radicles introduced in the following manner :—

In the case of naphthalene, express the position of the radicles introduced in place of hydrogen relatively to the carbon-atoms common to the two "rings," and number the positions in the one ring 1, 2, 3, 4, and those in the other 1′, 2′, 3′, 4′ in the order shown by the annexed symbol :—

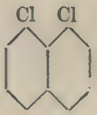


The dichloronaphthalenes, for example, are spoken of simply as 1 : 2 dichloronaphthalene, or dichloronaphthalene [Cl : Cl = 1 : 2], &c., thus :—

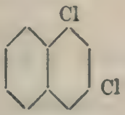
1 : 2 dichloro-naphthalene =



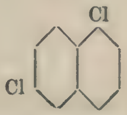
1 : 1′ dichloro-naphthalene =



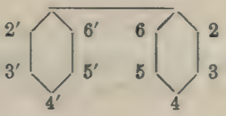
1 : 3 dichloro-naphthalene =



1 : 3′ dichloro-naphthalene =

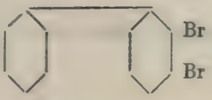


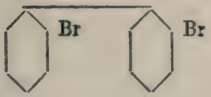
In the case of diphenyl, indicate the position of the radicles relatively to the carbon-atom of one C_6 group which is associated with the other C_6 group, and number the positions in the one group by the figures 2, 3, 4, 5, 6, and the corresponding positions in the other group by the figures 2′, 3′, 4′, 5′, 6′, as shown by the following symbol :



Thus the mono-derivatives, the bromodiphenyls, for example, are represented as

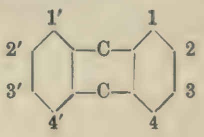
Bromodiphenyl [Br = 2]
" [Br = 3]
" [Br = 4]

and the two dibromodiphenyls  and

 are respectively dibromodiphenyl [Br : Br = 2 : 3]

and dibromodiphenyl [Br : Br = 2 : 6′].

In the case of anthracene, employ the following symbol and indicate the position of the radicles relatively to the central C_2-group :



Examples :

Alizarin, $C_6H_4\colon C_2O_2\colon C_6H_2(OH)_2$ [OH : OH = 1 : 2].
Quinizarin, $C_6H_4\colon C_2O_2\colon C_6H_2(OH)_2$ [OH : OH = 1 : 4].
Anthraflavic acid, $C_6H_3(OH)\colon C_2O_2\colon C_6H_3(OH)$ [OH : OH = 2 : 3′].

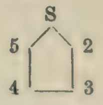
Purpurin, $C_6H_4\colon C_2O_2\colon C_6H(OH)_3$ [OH : OH : OH = 1 : 2 : 4].

In speaking of compounds such as these, their constitution may be represented by the names

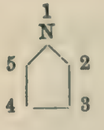
1 : 2 Dihydroxyanthraquinone = Alizarin.
1 : 4 ,, = Quinizarin.
2 : 3′ ,, = Anthraflavic acid.
1 : 2 : 4 Trihydroxyanthraquione = Purpurin.

Always include the letters and figures indicating the constitution of derivatives of closed-chain hydrocarbons in square brackets.

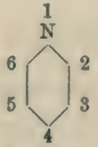
21. *In the case of thiophen*, express the position of the radicles introduced relatively to the sulphur atom by numbers, as shown by the following symbol :



In the cases of pyrroline and pyridine, indicate the position relatively to the nitrogen atoms as shown by the following symbols :

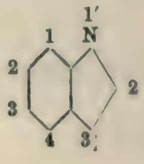


Pyrroline.

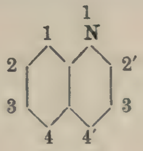


Pyridine.

In the case of indole, positions should be numbered as shown in the following symbol :—



In the case of quinoline, express the positions relatively to the carbon-atoms common to the two rings, and number the positions in the carbon ring 1, 2, 3, 4, and those in the nitrogen ring 1′, 2′, 3′, 4′, in the order shown by the annexed symbol :—



The Editor's decision, in all matters connected with the Abstracts, must be considered final.

JOURNAL

OF

THE CHEMICAL SOCIETY.

ABSTRACTS OF CHEMICAL PAPERS PUBLISHED IN BRITISH AND FOREIGN JOURNALS.

PART I.

Organic Chemistry.

Mixed Trimethylene Compounds. By LOUIS HENRY (*Compt. rend.*, 1896, **123**, 311—313).—The author has prepared some new trimethylene compounds by taking advantage of the different reaction aptitudes of the various halogens in mixed haloid derivatives (Abstr., 1883, 787).

Trimethylenic chloriodide, $CH_2Cl\cdot CH_2\cdot CH_2I$, is obtained by the action of trimethylenic chlorobromide on a molecular proportion of sodium iodide in presence of methylic alcohol. It is a colourless liquid which has a piquant odour, becomes brown when exposed to light, solidifies in solid carbonic anhydride and ether, forming crystals which melt at −69·5°, and boils at 170—172° under ordinary pressure; sp. gr. = 1·904 at 20°; vapour density = 6·98 (calc. = 7·06). The boiling point of this compound is exactly the mean of the boiling points of trimethylenic dichloride, 120°, and trimethylenic di-iodide, 224°.

Trimethylenic nitroxychloride, $CH_2Cl\cdot CH_2\cdot CH_2\cdot NO_2$, obtained by the action of the preceding compound on silver nitrate, is a colourless mobile liquid with a faint ethereal odour and piquant taste; sp. gr. = 1·267 at 20°. It does not solidify in solid carbonic anhydride and ether, boils and decomposes slightly at 197° under ordinary pressure, and boils at 115—116° under a pressure of 40 mm.; vapour density, 4·13 (calc. 4·26). C. H. B.

Preparation of Cyanogen Bromide, Bromonitromethane and Dibromonitromethane. By ROLAND SCHOLL (*Ber.*, 1896, **29**, 2325). Compare Abstr., 1896, i, 585. Reply to Tscherniac (Abstr., 1896, i, 661 .

Preparation of Ammonium Ferricyanide. By N. Tarugi (*Gazzetta*, 1896, **26**, ii, 25—28).—Silver ferricyanide, precipitated from potassium ferricyanide solution, is well washed and treated with the corresponding quantity of ammonium chloride; the filtrate, evaporated after filtering off the silver chloride, yields pure ammonium ferricyanide. If a standard solution of potassium ferricyanide is precipitated with standard silver nitrate, and standard ammonium chloride used to decompose the silver salt, an accurately standardised solution of ammonium ferricyanide can be obtained.

Bette (*Annalen*, 1837, **23**, 1) describes ammonium ferricyanide as crystallising in ruby red prisms which are stable in the air; it is really obtained in tiny green crystals which become blue in the air, although its solutions are very stable if preserved in closed vessels.

W. J. P.

Ferricyanides, and their Use as Oxidising Agents. By Georg Kassner (*Arch. Pharm.*, 1896, **234**, 330—348).—Although a solution of potassium ferricyanide containing potassium hydroxide in addition is stable in the dark, it is partly decomposed when heated above 60°, or when exposed to direct sunlight; under these circumstances ferric hydroxide is deposited, and the solution contains hydrocyanic acid and ammonia; the decomposition is less when an alkali carbonate is present in place of the hydroxide, still less in the presence of an alkali hydrogen carbonate. An alkaline solution of the ferrocyanide hardly undergoes any such change when heated, and does not undergo it at all when it is exposed to light, except when air is not excluded. The author says that the view of these double cyanides as salts of ferri- and ferro-cyanic acids must be given up; they are to be regarded as double salts in the old sense of the word, and in solution in excess of caustic alkali they are dissociated into the alkaline cyanide and colloidal ferric, or ferrous, hydroxide. When the ferricyanide acts as an oxidising agent, this ferric hydroxide is converted into ferrous hydroxide, which then forms ferrocyanide with the alkali cyanide present, the impetus to the whole series of reactions being found in the great tendency of alkali cyanides to form ferrocyanides with iron in any form. The spontaneous decomposition of the ferricyanide above 60° or in direct sunlight is explained by supposing that under these circumstances the colloidal ferric hydroxide is converted into the insoluble variety and precipitated; some of the alkali cyanide present is then hydrolysed by the water.

In order, therefore, to obtain a permanent alkaline ferricyanide bath, for oxidising or bleaching purposes, the temperature should be kept below 60° and light should be excluded; further, an excess of caustic alkali above the amount required by the equation should be avoided. To be regenerated, the bath should be treated with calcium plumbate (best already converted into calcium carbonate and lead dioxide), and carbonate anhydride passed in. Potassium carbonate is formed at the same time, but this can be removed by adding calcium plumbate, which is decomposed in the process into calcium carbonate and lead dioxide, the mixture required for the operation described above.

C. F. B.

Action of Morphine and of Acetanilide on Mixtures of Ferric Salts and Ferricyanides. By EDUARD SCHAER (*Arch. Pharm.*, 1896, **234**, 348—367).—Morphine reduces both ferric chloride and potassium ferricyanide, the former more strongly in neutral, the latter more strongly in acid solution. As a result of its action on a mixture of the two, a green coloration and, eventually, a blue precipitate are obtained. This precipitate consists mainly of Prussian blue, although it contains a little Turnbull's blue; on the whole, therefore, the ferricyanide has been reduced in preference to the ferric chloride.

Acetanilide also reduces both ferric chloride and potassium ferricyanide, but less strongly than morphine does. The precipitate that it produces in a cold neutral mixture of the two consists chiefly of Turnbull's blue; if the solution is hot, or if it is acid, however, Prussian blue is formed in larger amount.

Neither morphine nor acetanilide produces a blue precipitate in a mixture of potassium ferricyanide with soluble (dialysed) ferric hydroxide or ferric acetate. C. F. B.

Fulminates. By ARNOLD F. HOLLEMAN (*Rec. Trav. Chim.*, 1896, **15**, 159—160).—The solubility of purified mercury fulminate in water is at 12° 0·693—0·710, at 49° 1·7381—1·7835 gram per litre. The solubility of silver fulminate is at 13° 0·075, at 30° 0·180 gram per litre. One property common to both sodium fulminate and sodium cyanate is that of dissolving silver and thus forming double salts of the type $NaCNO,AgCNO$. J. J. S.

The Influence of the Presence of Acids on the Oxidation of Alcohols. By ANDRÉ BROCHET (*Bull. Soc. Chim.* [3], 1896, **15**, 16—20).—When treated with chlorine, isobutylic alcohol has been shown to give a chlorisobutaldehyde which, in presence of the hydrogen chloride formed during the reaction, condenses with the alcohol present in excess.

In order to eliminate the effect of the hydrogen chloride, the author treated a 10 per cent. aqueous solution of the alcohol with chlorine until no more of the gas was absorbed; the oil which separated on the surface of the water was found to contain isobutylic isobutyrate mixed with excess of the unaltered alcohol. After prolonged treatment with chlorine, the chlorinated derivatives of this salt appeared to be formed, particularly the α-chloro-compound, a liquid which boils at 183°, has sp. gr. = 0·998 at 15°/4°, refractive index $n_D = 1·435$ at 17°; on treatment with alkalis, this breaks up into isobutylic alcohol, and either α-chlorisobutyric acid, α-hydroxybutyric acid, or α-methylacrylic acid, according to the conditions of the reaction. The aqueous solution was found to contain a mixture of these acids with acetone and acetic and formic acids.

When the liquid was kept nearly neutral by the addition of sodium carbonate, isobutylic isobutyrate was formed as before, but the α-chloro-derivative and acetone only in very small quantity. Isobutylic alcohol in contact with a solution of sodium hypochlorite was found to yield 25 per cent. of the ethereal salt at the end of two months.

Lieben has obtained similar results with ethylic alcohol. Chlorine reacts with a mixture of alcohol, water, and potassium carbonate, producing chloroform and ethylic acetate. When there is little or no water present, ethylic acetate is almost the sole product of the reaction. Bromine gives the same result. From these results it would appear that chlorine or bromine, acting on an alcohol in neutral or very slightly acid solution, behaves as an oxidising agent, and does not tend to displace hydrogen atoms in the molecule.

The conditions necessary for the production of aldehydes from alcohol by the aid of acid oxidising agents are also discussed.

M. W. T.

Action of Chlorine on Hot Isobutylic Alcohol. By André Brochet (*Bull. Soc. Chim.*, 1896, [3], **15**, 20—22).—The reaction is extremely complicated, but, as long as there is excess of the alcohol present, the chief product appears to be the compound $CMe_2Cl\cdot CH(OC_4H_9)_2$. On further chlorination, however, this breaks up into α-chlorisobutaldehyde and α-chlorisobutylic isobutyrate. Isobutyric acid, hydroxyisobutyric acid, chlorisobutyric acid, and α-methylacrylic acid are also products of the reaction.

If the action of the chlorine is prolonged, dichlorisobutaldehyde, boiling at 123°, is obtained together with isobutylic dichlorisobutyrate, which boils at 229° and has a sp. gr. = 1·155 at 15°/4°. Hexachlorethane appears to be one of the final products of the reaction. M. W. T.

Crystallised d-Mannose. By W. Alberda van Ekenstein (*Rec. Trav. Chim.*, 1896, **15**, 221—224. Compare Abstr., 1896, i, 272). —The author has studied the chief physical properties of crystallised *d*-mannose prepared by the decomposition of its phenylhydrazone by benzaldehyde (compare Abstr., 1895, i, 260). The pure syrupy *d*-mannose thus obtained was dissolved in various solvents, and the small crystals which separated after several weeks from a mixture of methylic alcohol and ether (1 : 1) were used for the purpose of inducing crystallisation in the other solutions. The substance thus obtained, after recrystallisation from 90 per cent. ethylic alcohol, melted at 132° without darkening, and was anhydrous, having the formula $C_6H_{12}O_6$. 100 parts of water at 17° dissolves 248 parts of *d*-mannose; 100 c.c. of absolute ethylic alcohol at 17·5° dissolves 0·4 gram. It has a somewhat bitter taste, and exhibits the property of multirotation. A 2 per cent. solution gave the following rotations:—After 3 minutes $[\alpha]_D = -13°\cdot 6$, after 6 hours (when constant) $[\alpha]_D = +14°\cdot 25$. The crystals are rhombic; $a : b : c = 0\cdot 319 : 1 : 0\cdot 826$.

The α-methylmannoside of E. Fischer was also examined; its solubility at 17° is, in water, 24·6 grams; in absolute alcohol, 1·5 gram; in 90 per cent. alcohol, 3·2 grams; in 80 per cent. alcohol, 7·8 grams per 100 c.c. of solvent. Its rotatory power in 1 per cent. aqueous solution is $[\alpha]_D = +82\cdot 5°$; in 8 per cent. solution, $+79\cdot 2°$; in 1 per cent. alcoholic solution, $+87\cdot 3°$. Its crystals are rhombic; $a : b : c = 0\cdot 9336 : 1 : 0\cdot 9249$.

The author has failed in his endeavours to prepare β-methylmannoside. A. C. C.

Decomposition of Monosaccharides by Alkalis. By FRIEDRICH FRAMM (*Pflüger's Archiv*, 1896, **64**, 575—599).—Moore's test is one of the best known of the monosaccharide reactions. Light has no influence on the decomposition. Equal molecular quantities of sodium or potassium hydroxide act in the same way on *d*-glucose. In the product, a considerable quantity of sugar is left, which may be estimated by Allihn's method; various products of oxidation (formic, acetic, oxalic, and especially lactic acids—Beilstein, Tollens), and certain brown products (glucic, saccharumic, japonic, and melassic acids) have been described.

The exclusion of air lessens the decomposition, and it is the products of oxidation with which this paper is specially concerned. In the case of *d*-glucose, only aldehyde and formic acid were identified among the products of oxidation. Galactose yields the same two substances. *d*-Fructose yields formic acid, and a doubtful trace of aldehyde. When air is excluded, *d*-fructose is more readily decomposed than *d*-glucose and galactose. Arabinose yields the same oxidation products as the hexoses. W. D. H.

Aldazines, Ketazines, and Benzosazones of Aldoses and Ketoses. By ERNST DAVIDIS (*Ber.*, 1896, **29**, 2308—2311. Compare Abstr., 1895, i, 33, and 216).—*Glucosealdazine*, $C_6H_{12}O_5\colon N\cdot N\colon C_6H_{12}O_5$, is obtained by heating finely-powdered glucose with hydrazine hydrate (2 mols.) and methylic alcohol, on the water bath; this being a general method for the production of aldazines and ketazines of sugars; it is a white, microcrystalline powder, and sinters about 80°, when it begins to decompose, melting indefinitely at 100°. It is very hygroscopic, dissolves readily in methylic alcohol and in water, the solution being neutral; it is insoluble in ether, chloroform, and benzene. The substance does not decompose in cold, aqueous solution, and is also indifferent towards dilute, aqueous alkalis; hydrolysis with dilute acids resolves it into glucose and hydrazine.

Arabinosealdazine, $C_5H_9O_4\colon N\cdot N\colon C_5H_9O_4$, closely resembles glucosealdazine, and is obtained from arabinose in a similar manner.

Fructoseketazine, $C_6H_{12}O_5\colon N\cdot N\colon C_6H_{12}O_5$, is a micro-crystalline, yellowish powder, which is less hygroscopic than the foregoing substances.

Glucosebenzosazone, $OH\cdot CH_2\cdot CH(OH)\cdot[C(\colon N\cdot NHBz)]_3\cdot CH\colon N\cdot NHBz$, is obtained when glucose is heated with benzhydrazide and very dilute caustic soda for 1½ hour on the water bath; it crystallises in yellowish-brown leaflets, and melts at 256—257°. Levulose gives rise to the same substance.

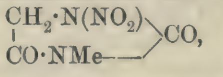
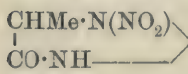
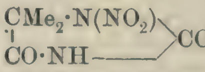
The author has observed that arabinosebenzhydrazide melts at 211—212° instead of 184°, and dextrosebenzhydrazide at 195—196° instead of 171—172° (compare Wolff, Abstr., 1895, i, 216).

M. O. F.

Composition of Wood Gum. By SAMUEL W. JOHNSON (*J. Amer. Chem. Soc.*, 1896, **18**, 214—222).—Wood gum is abundantly extracted from the wood of deciduous trees by cold, weak (2—10 per cent.) solutions of sodium hydroxide, and is thrown down again on neutralisation or on the addition of alcohol. On hydrolysis, it yields xylose. Wheeler and Tollens (*Annalen*, **254**, 320), &c., gave the formula $C_6H_{10}O_5$ for wood gum. The author shows by means of numerous analyses that wood gum obtained from ground maize cob is really the anhydride of xylose, that is, it is xylan, and has the composition $C_5H_8O_4$. The analysis is an extremely difficult operation as the compound has such a great avidity for water; the hygroscopic moisture is best determined by heating the substance to 110—112° in a vacuum.

The wood gum obtained from the American white or grey birch (*Betula alba*) has the composition $C_4H_6O_3$, and does not yield xylose on hydrolysis. This compound and its products of hydrolysis are being further investigated.

Dilute alkali extracts from vegetable ivory a substance similar to wood gum, which when hydrolysed yields mannose (compare Reiss, *Ber.*, 1889, **22**, 609), and, according to the author, has the composition $C_6H_{10}O_5$. He terms it mannan, and it is beyond doubt identical with Reiss's seminin and Tollens's paramannan. J. J. S.

Action of Alkalis on Neutral Aliphatic Nitramines. By Antoine P. N. Franchimont and H. Van Erp (*Rec. Trav. Chim.*, 1896, **15**, 165—173. Compare Van Erp, Abstr., 1895, i, 590). When nitrohydantoïn is treated with baryta water, it yields nitrous acid and other products, but not nitraminoacetic acid as the authors expected. Nitromethylhydantoïn,  $\begin{matrix}CH_2\cdot N(NO_2)\\ |\\ CO\cdot NMe\end{matrix}\!\!>\!CO$, and nitrolactylcarbamide,  $\begin{matrix}CHMe\cdot N(NO_2)\\ |\\ CO\cdot NH\end{matrix}\!\!>\!CO$, also yields nitrous acid under similar treatment, whereas nitroacetonylcarbamide,  $\begin{matrix}CMe_2\cdot N(NO_2)\\ |\\ CO\cdot NH\end{matrix}\!\!>\!CO$, gives no trace of nitrous acid even after boiling with baryta water. It thus appears that in order to yield nitrous acid, the nitramine must have an atom of hydrogen attached to the carbon atom to which the nitramine group is directly united.

The authors have prepared *butylmethylenimine*, $C_4H_9N\!:\!CH$, by Henry's method (*Bull. Acad. R. Belg.*, 26—29, 1893—1895). Normal butylamine dissolved in an equal volume of water was added to a cold 40 per cent. solution of methanal; an oily liquid of sp. gr. 0·886 at 15° was thus obtained, which is probably *butylaminomethylic alcohol*, $C_4H_9\cdot NH\cdot CH_2\cdot OH$. It cannot be distilled without undergoing decomposition, and when treated with cold aqueous potash, it yields butylmethylenimine; this distils at 146—149° (10—12 mm.), and has a sp. gr. = 0·8772 at 15°. It combines in the cold with sulphuric acid, and the solution thus obtained when diluted yields methanal; nitrosyl sulphate, however, has no action on the compound. The imine yields a white precipitate with mercuric chloride and a silver mirror with silver nitrate, it precipitates the hydroxides from ferric chloride and copper sulphate solutions, and it combines with oxalic and picric acids. When reduced with sodium and alcohol, it yields primary butylamine, and methylbutylamine (?), and when heated with potash and water at 150° for 6 hours, it yields formic acid and butylamine. These facts support Erp's views (Abstr., 1895, i, 590) regarding the action of alkalis on nitramines. Thus, on heating with potassium hydroxide, the nitramine is first decomposed into nitrous acid and an imine, but the latter undergoes further decomposition into a primary amine and formaldehyde; this, however, by the action of the alkali, is converted into formic acid. J. J. S.

Methylallylnitramine, an Isomeride, and their Bromine Derivatives. By HERM. UMBGROVE and ANTOINE P. N. FRANCHIMONT (*Rec. Trav. Chim.*, 1896, **15**, 195—210).—The chief object of this research was to ascertain whether a mixed nitramine of the general formula $RR'N\cdot NO_2$ containing one unsaturated radicle would resemble in its general properties a nitramine containing an aromatic radicle on the one hand, or one containing two alkyls on the other, the former bearing a much closer resemblance than the latter to the nitramides, on account of the more negative character of the aromatic radicle. Caustic alkalis, for instance, cause the separation of the benzyl group from the nitrogen in methylbenzylnitramine, whilst in methylethyl- and methylbutyl-nitramine the alkyl groups are not affected.

Methylallylnitramine, $CH_2{:}CH\cdot CH_2\cdot NMe\cdot NO_2$, was prepared both by the action of the potassium derivative of methylnitramine on allylic iodide and also by heating a mixture of potassium hydroxide, methylnitramine and allylic bromide, methylic alcohol being employed as a solvent in both methods. It is a colourless, refractive liquid, boils at 95—96° (18 mm.), decomposes when distilled under atmospheric pressure, has sp. gr. 1·1015 at 15°, and is almost insoluble in water, but soluble in all the ordinary organic solvents. When it is heated with an aqueous solution of potassium hydroxide in a sealed tube, nitrous acid, methylamine and an aldehyde, probably acraldehyde, are formed. It therefore behaves like benzylmethylnitramine, and not like a nitramine containing only alkyl groups.

The authors consider it very probable that methylallylenimine, $CH_2{:}CH\cdot CH{:}NMe$, is first formed together with nitrous acid in this reaction, and that this then gives rise under the influence of alkali and water to acraldehyde and methylamine. The above imine could not, however, be isolated (compare preceding abstract).

On oxidation with silver oxide, methylallylnitramine yielded nitrous acid, methylamine and probably acrylic acid; with weak aqueous potassium permanganate, it was hoped that a *methyldihydroxypropylnitramine* would be obtained; this was not isolated, but its *dibenzoate*, $OBz\cdot CH_2\cdot CH(OBz)\cdot CH_2\cdot NMe\cdot NO_2$, crystallised from ether in colourless needles, melting at 102°.

Methylallylnitramine combines with bromine in chloroform solution forming *methyl*-2 : 3-*dibromopropylnitramine*, a liquid of sp. gr. = 1·945 at 15°, which on cooling crystallised in large, monoclinic crystals, melting at 23°. It is insoluble in water, but dissolves in all the ordinary organic solvents. Attempts to convert this by hydrolysis into the dihydroxy-compound failed, although a small quantity of its dibenzoate, above described, was obtained.

From the lower fractions obtained during the fractional distillation of the products of the action of allylic bromide on the potassium derivative of methylnitramine, an isomeride of methylallylnitramine was obtained boiling at 51—52° (18—20 mm.). It is a colourless, mobile liquid, having a powerful odour, and of sp. gr. = 1·047 at 15°. It is distinguished from methylallylnitramine by its lower boiling point, lower specific gravity and by its different behaviour with caustic alkalis and sulphuric acid. When heated in a sealed tube with a solution of potassium hydroxide, it yields allylic alcohol and a gas, which probably is nitrogen. In the reaction of allylic bromide or iodide with the silver derivative of methylnitramine, both these isomeric nitramines were obtained in about equal proportions. This isomeride combines with 2 atoms of bromine in chloroform solution, yielding a substance which crystallises in colourless needles, melting at 65°, isomeric with the dibromo-derivative above described (compare following abstract). A. C. C.

Methylnitramine, Dimethylnitramine, and one of its Isomerides. By ANTOINE P. N. FRANCHIMONT aud HERM. UMBGROVE (*Rec. Trav. Chim.*, 1896, **15**, 211—220).—The observation that methylnitramine which has been somewhat strongly heated loses to some extent its power of crystallising readily, induced the authors to study the action of heat on that substance. When submitted to distillation, the temperature rises from below 100° to 187°, the products obtained being nitrous oxide, methylic alcohol, water, an isomeride of dimethylnitramine and dimethylnitramine (b. p. 187°) itself. The isomeride is distinguished from dimethylnitramine by its boiling point (112°), by its behaviour with strong sulphuric acid, with which it reacts vigorously, and by producing an immediate coloration in an acetic acid solution of *a*-naphthylamine. The quantitative relations between the above products were so dependent on the conditions under which the heating was effected, that it is impossible to represent the change by means of an equation; moreover, small quantities of nitrogen and of an oil (? a pyridine base) were also formed. The mechanism of this change is discussed, but the authors are unable at present to suggest any satisfactory explanation. By the action of methylic iodide on the silver derivative of methylnitramine, two dimethylnitramines are formed, one being the ordinary compound (b. p. 187°), whilst the other is apparently identical with the isomeride above mentioned (b. p. 112°). Its sp. gr. = 1·079 at 20°. The isomeric nitramine, when heated with an aqueous solution of potassium hydroxide in a sealed tube, yields methylic alcohol and nitrogen. (Compare preceding abstract for an analogous decomposition of the isomeride of allylmethylnitramine.) The authors suggest provisionally that the formula of the isomeric methylnitramine is $NMe\vdots NO\cdot OMe$. A. C. C.

Action of Alkylic Iodides on Hydroxylamine. By CORNELIS A. LOBRY DE BRUYN (*Rec. Trav. Chim.*, 1896, **15**, 185—186. Compare Abstr., 1894, i, 569).—The author confirms Dunstan's statement (Dunstan and Goulding, Proc., 1896, 72) that the product obtained by the action of methylic iodide on hydroxylamine consists of trimethylhydroxylamine hydriodide and two hydriodides of hydroxylamine.

J. J. S.

Nitracetonitrile. By Roland Scholl (*Ber.*, 1896, **29**, 2415—2421).—Attempts to synthesize nitracetonitrile by the action of cyanogen bromide on sodium nitromethane having resulted in the production of bromonitromethane, the behaviour of iodacetonitrile towards silver nitrite has been studied.

Iodacetonitrile is conveniently prepared by heating chloracetonitrile (112 grams) with finely-powdered potassium iodide (300 grams) and methylic alcohol (300 grams) for 3 hours on the water bath. It is a heavy, colourless oil, which boils, and in part decomposes, at 182—184° under a pressure of 720 mm. When it is treated with silver nitrite, action occurs spontaneously, being accompanied by very rapid rise of temperature; if the mixture is cooled, it proceeds slowly, and a yellow double salt of silver iodide with an organic substance is produced, yielding a volatile oil when treated with boiling water.

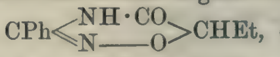
Cyanomethazonic acid, $C_4H_2N_4O_3$, is obtained by adding, in small quantities at a time, a mixture of silver nitrite and sand to a hot solution of iodacetonitrile in benzene; it is a viscous, yellowish oil, and boils at 160—162° (uncorr.) under a pressure of 12 mm. The substance explodes when rapidly heated under atmospheric pressure, and the action of concentrated hydrochloric acid in sealed tubes at 60° gives rise to considerable quantities of ammonium chloride and oxalic acid, along with a small proportion of hydroxylamine; concentrated sulphuric acid liberates nitrous oxide, and, on warming the liquid, carbonic anhydride and carbonic oxide are produced, probably arising from oxalic acid. Fuming nitric acid dissolves the substance, and is without action on it when boiled. Cyanomethazonic acid dissolves readily in alkalis, but is not precipitated when the solution is rendered acid; thus dilute sulphuric acid causes the liquid to effervesce, and liberates hydrogen cyanide, ether extracting an oil which deposits crystals melting at 105—107°. When alcoholic sodium ethoxide is added to a solution of cyanomethazonic acid in absolute alcohol, sodium nitrite is precipitated, and benzylamine added to a solution of it in benzene gives rise to benzylamine nitrite.

The *compound*, $C_6H_4N_4O_2$, is produced when cyanomethazonic acid is heated with boiling water in a reflux apparatus during many hours, and also occurs as a bye-product in the preparation of that substance; it melts at 72°, and forms white crystals resembling ammonium chloride. It is insoluble in carbon bisulphide and petroleum, but dissolves readily in acetone, and sparingly in water, alcohol, ether and chloroform. Soda dissolves it readily when heated, but it is not thrown down from this solution by acids, these causing effervescence, and liberating hydrogen cyanide. Cold concentrated sulphuric acid dissolves the substance, generating heat in the process; oxalic acid is subsequently found in the solution. M. O. F.

α-Hydroxylaminebutyric Acid. By Alfred Werner and R. Falck (*Ber.*, 1896, **29**, 2654—2659. Compare Abstr., 1893, i, 501; 1895, i, 125, 521).—When ethylic α-bromobutyrate (1 mol.) and benzenylamidoxime (1 mol.) are warmed together in presence of alkali (2 mols.), condensation takes place with production of derivatives of benzenylamidoximebutyric acid, namely, its potassium and ethylic salts and its esoanhydride. These are separable by means of alkali, which leaves the ethylic salt undissolved, and if hydrochloric acid be subsequently added to the alkaline liquid, the esoanhydride is precipitated, the acid itself dissolving in excess of hydrochloric acid.

Ethylic benzenylamidoximebutyrate, $NH_2\cdot CPh\colon N\cdot O\cdot CHEt\cdot COOEt$, is a white substance melting at 57°; it is readily soluble in alcohol, ether and benzene, but insoluble in water and light petroleum.

Benzenylamidoximebutyric acid, $NH_2\cdot CPh\colon N\cdot O\cdot CHEt\cdot COOH$, is most readily obtained by hydrolysis of the foregoing ethylic salt; it forms white crystals, melting at 81—82°, is very sparingly soluble in water, more readily in petroleum and benzene, and is readily soluble in alcohol and ether. The *hydrochloride*, $C_{11}H_{15}N_2O_3Cl$, is formed by the action of concentrated hydrochloric acid on the esonahydride at 100—120°; it separates from water in prismatic crystals, melting at 148°, and is readily soluble in water and alcohol, but insoluble in most organic media.

Benzenylamidoximebutyric anhydride,  $CPh<\begin{matrix}NH\cdot CO\\ N\text{———}O\end{matrix}>CHEt$, crystallises in prisms melting at 106°, and is insoluble in cold water, but dissolves readily in alcohol, ether, and benzene.

Benzenylchloroximebutyric acid, $CPhCl\colon N\cdot O\cdot CHEt\cdot COOH$, is obtained by the action of sodium nitrite on the solution of the hydrochloride of the above acid, and crystallises in colourless needles or leaflets melting at 77°. It is practically insoluble in water, but dissolves readily in alcohol, ether, benzene, and acetic acid. The corresponding *benzenylbromoximebutyric acid*, $CPhBr\colon N\cdot O\cdot CHEt\cdot COOH$, melts at 68·5°. *Ethylbenzhydroximebutyric acid*,

$$OEt\cdot CPh\colon N\cdot O\cdot CHEt\cdot COOH,$$

is formed by the action of sodium ethoxide on the foregoing chloroderivative; it crystallises in colourless needles, melts at 72°, dissolves readily in alcohol, ether, and benzene, but is insoluble in water. *Methylbenzhydroximebuytric acid*, $OMe\cdot CPh\colon N\cdot O\cdot CHEt\cdot COOH$, melts at 68°.

The *hydrochloride* of hydroxylaminebutyric acid,

$$COOH\cdot CHEt\cdot O\cdot NH_2,HCl,$$

is made by evaporating to dryness on the water bath a solution of ethylbenzhydroximebutyric acid in dilute hydrochloric acid; it melts at 165·5°, crystallises from water, in which it is readily soluble, and is sparingly dissolved by alcohol. *a-Hydroxylaminebutyric acid*,

$$COOH\cdot CHEt\cdot ONH_2,$$

is prepared from its hydrochloride by the action of silver hydroxide, subsequent treatment with hydrogen sulphide serving to decompose the resulting silver salt; it is a white substance, readily soluble in water and in alcohol, but insoluble in ether and light petroleum; it melts at 156°. A. L.

Solubilities of Salts of Caproic and of Œnanthylic Acids. By Emil Altschul (*Monatsh.*, 1896, 17, 567—578. Compare Abstr., 1895, ii, 7).—As the results of determinations of the solubilities of the calcium and silver salts of hexoic (caproic) and of heptoic (œnanthylic) acid do not agree with the generalisations which Lieben has found to exist among the salts of other fatty acids, the author has re-determined these solubilities.

Deszáthy's filtering apparatus was used, and the determinations were made both by the method of "cooling" and of "warming."

The solubility of silver hexoate agrees with the formula

$$L = 0{\cdot}07802 + 0{\cdot}0003335(t - 0{\cdot}5^\circ) + 0{\cdot}000040136(t - 0{\cdot}5^\circ)^2.$$

The solubility of calcium hexoate at temperatures between 0° and 47° agrees with the formula $L = 2{\cdot}713 - 0{\cdot}01627t + 0{\cdot}0001257t^2$; and for temperatures between 47° and 70·5° the expression $L = 2{\cdot}226 + 0{\cdot}02335(t - 47^\circ) - 0{\cdot}0001517(t - 47^\circ)^2$ holds good. The numbers obtained by the author for these two salts agree with those obtained by Keppich (Abstr., 1889, 122).

The numbers obtained in the case of silver heptoate fall far below those obtained by Landau for the same salt (Abstr., 1894, i, 226). The formula given is $L = 0{\cdot}04492 + 0{\cdot}0006416(t - 2^\circ) - 0{\cdot}00000957(t - 2^\circ)^2 + 0{\cdot}0000002905(t - 2^\circ)^3$. The solubility of calcium heptoate between 0·5° and 47·5° is $L = 0{\cdot}9015 - 0{\cdot}00199007(t - 0{\cdot}5^\circ) + 0{\cdot}000001702(t - 0{\cdot}5^\circ)^2$; and between 47·5° and 77·5°

$$L = 0{\cdot}7923 + 0{\cdot}0020102(t - 47{\cdot}5^\circ) + 0{\cdot}00002056(t - 47{\cdot}5^\circ)^2.$$

J. J. S.

Derivatives of Arachidic Acid. By MAX BACZEWSKI (*Monatsh.*, 1896, 17, 528—546).—*a-Bromarachidic acid*, $C_{20}H_{39}BrO_2$ is obtained when arachidic acid is treated with bromine in presence of amorphous phosphorus; it forms white, silky crystals, melts at 62—64°, and dissolves readily in alcohol, ether, light petroleum and chloroform. The *ethylic* salt dissolves readily in ether, light petroleum and chloroform and crystallises in microscopic needles melting at 37—39°; the *methylic* salt has similar properties and melts at 33—35°. The *sodium* salt, $C_{20}H_{38}BrO_2Na$, *calcium*, *copper* and *silver* salts are described.

a-Iodarachidic acid, $C_{20}H_{39}IO_2$, is prepared by the action of potassium iodide on the foregoing acid; it crystallises in small, white prisms and melts at 70°; the *silver* salt is a yellow powder.

A small quantity of an unsaturated acid is formed when arachidic acid is heated with bromine and water in a sealed tube at 170°.

a-Hydroxyarachidic acid, $C_{20}H_{40}O_3$, is formed from a-bromarachidic acid when it is heated with alcoholic soda during 20 hours; it forms silky leaflets melting at 91—92°. The *ethylic* salt is soluble in alcohol, ether, etc., and crystallises in aggregations of needles melting at 62—66°; the *methylic* salt forms slender, white needles, and melts at 62—64°.

a-Ethoxyarachidic acid, $C_{22}H_{44}O_3$, is obtained by heating the hydroxy-acid with sodium ethoxide; it crystallises in slender needles, dissolves in the ordinary media and melts at 53—56°, its *ethylic* salt, $C_{24}H_{48}O_3$, crystallises in attenuated needles and melts at 35—37°; the *sodium*, *barium*, and *lead* salts are described.

a-Amidoarachidic acid, $C_{20}H_{41}NO_3$, results from the action of *a*-

bromarachidic acid on ammonia at 140°; it is very sparingly soluble in hot alcohol, more readily in hot acetic acid, but is insoluble in ether, petroleum, benzene, chloroform and strong hydrochloric acid; it darkens and melts at 212—214°, evolving gases, and the residue remains fluid at 40°. It is not identical with the acid obtained by Tassinari (Abstr., 1879, 307) on reducing nitroarachidic acid, as the former yields metallic salts whilst the latter does not; the *sodium* salt, $C_{20}H_{40}NO_2Na$, is a white, crystalline powder sparingly soluble in alcohol, whilst the *calcium* salt, $(C_{20}H_{40}NO_2)_2Ca$, is amorphous.

When α-bromarachidic acid is heated at 180°, with excess of aniline, during 7 hours, *α-anilidoarachidanilide*, $C_{32}H_{50}N_2O$, is obtained; it crystallises in amorphous grains melting at 82°, and is readily soluble in alcohol, benzene, petroleum, chloroform, and acetic acid, but is not dissolved by alkalis. If the temperature of the original mixture is maintained at 140° during 1 hour only, *α-anilidoarachidic acid*, $C_{26}H_{45}NO_2$, is produced. The latter dissolves sparingly in alcohol, readily in acetic acid and chloroform, but is insoluble in petroleum; it melts at 138—139°.

α-Cyanarachidic acid may be prepared by boiling an alcoholic solution of the bromo-acid with potassium cyanide during 5 days; it separates from alcohol as a white, crystalline powder, melts at 88°, and evolves gases at about 170°; when boiled with potash, it evolves ammonia and yields a mixture of two acids which may be separated by means of ether; the insoluble portion consists of *octodecylmalonamic acid*

$$C_{18}H_{37}\cdot CH(CONH_2)\cdot COOH,$$

which crystallises from acetic acid and melts with effervescence at 126°. The soluble fraction contains *octodecylmalonic acid*,

$$C_{18}H_{37}\cdot CH(COOH)_2.$$

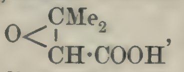
The latter is finally crystallised from petroleum (whereby a more readily soluble substance melting at 70—80° is eliminated) and is then obtained in white, crystalline granules melting at 109—110°; it decomposes, evolving carbonic anhydride, at 124—170°, and the residue subsequently melts at 73°.

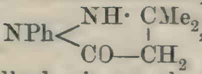
Arachidamide, $C_{20}H_{41}NO$, melts, as asserted by Fileti and Ponzio (compare Abstr., 1894, i, 13) at 108°. *Arachidanilide*, $C_{26}H_{45}NO$, may be obtained in a pure condition by heating arachidic acid and aniline together at 200°; it crystallises from alcohol in long, felted needles and melts at 96°. A. L.

Derivatives of Dimethylacrylic Acid. By Bertram Prentice (*Annalen*, 1896, **292**, 272—295. Compare Abstr., 1895, i, 17).—*Ethylic αβ-dibromisovalerate* is obtained by the action of bromine dissolved in carbon bisulphide on ethylic dimethacrylate (compare Ariff, *loc. cit.*, 16); it is a liquid of sp. gr. = 1·1652 at 17°/4°, having an agreeable odour of peppermint, and boils at 127—128° under a pressure of 30 mm.

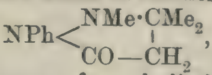
Chlorhydroxyisovaleric acid, $OH\cdot CMe_2\cdot CHCl\cdot COOH$, is prepared from dimethacrylic acid by means of hypochlorous acid, and crystallises in colourless plates; the *calcium* and *barium* salts contain $2H_2O$, whilst the *cadmium*, *zinc*, and *copper* salts are anhydrous.

Chlorodimethacrylic acid, $CMe_2{:}CCl\cdot COOH$, is produced when concentrated sulphuric acid acts on chlorhydroxyisovaleric acid, and it crystallises from water in white needles melting at 85—86°; the *calcium* salt contains $4H_2O$, and crystallises in large, rhombohedral prisms, whilst the *strontium* salt, which also contains $4H_2O$, crystallises in needles and plates. The *barium* and *cadmium* salts are also crystalline, the *magnesium* salt contains $3\frac{1}{2}H_2O$, the *lead* salt $2H_2O$, and the *silver* salt crystallises in long, slender needles.

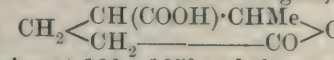
ββ-Dimethylglycidic acid,  $O{<}\begin{array}{l}CMe_2\\ \mid\\ CH\cdot COOH\end{array}$, is obtained from chlorhydroxyisovaleric acid by elimination of hydrogen chloride with alcoholic potash; although the acid has not yet been obtained in crystals, the *potassium* salt, containing $\frac{1}{2}H_2O$, forms colourless plates, and the *silver* salt crystallises from hot water in small plates,

1-*Phenyl-3-dimethyl-5-pyrazolidone*,  $NPh{<}\begin{array}{l}NH\cdot CMe_2\\ \quad\mid\\ CO{-}CH_2\end{array}$, is produced when dimethacrylic acid and phenylhydrazine are heated at 115° in the oil-bath, the temperature being subsequently raised to 175°; it crystallises in stellar aggregates of colourless needles, and melts at 74·5—75°. The *hydrochloride* forms microscopic needles. The *acetyl*-derivative melts at 104·5—105°, and crystallises in large, six-sided prisms; the *nitroso*-derivative is an unstable substance, and is very readily soluble in common solvents.

β-Phenylazoisovaleric acid, $NPh{:}N\cdot CMe_2\cdot CH_2\cdot COOH$, is formed when the foregoing substance is heated with baryta in a reflux apparatus; it crystallises from glacial acetic acid in long prisms, and melts at 57·5—58°. The *silver* salt crystallises from hot water in needles.

1-*Phenyl*-2 : 3 : 3-*trimethyl-5-pyrazolidone*,  $NPh{<}\begin{array}{l}NMe\cdot CMe_2\\ \quad\mid\\ CO{-}CH_2\end{array}$, is obtained from the pyrazolidone derivative by means of methylic iodide; the *hydrochloride* crystallises in needles. M. O. F.

General Synthetical Method for the Preparation of γδ-Unsaturated Acids.—By FRITZ FICHTER (*Ber.*, 1896, **29**, 2367—2372).—γδ-Unsaturated acids can readily be obtained by the distillation of δ-lactone-γ-carboxylic acids; this reaction is analogous to that used by Fittig in the preparation of βγ-unsaturated acids, namely by the distillation of γ-lactone-β-carboxylic acids (paraconic acids). The δ-lactone-γ-carboxylic acids are best obtained by the reduction of the corresponding dibasic ketonic acids or of their ethereal salts (compare Gantter, *Diss.*, 1878).

Ethylic acetylglutarate, $COOEt\cdot CHAc\cdot CH_2\cdot CH_2\cdot COOEt$, when reduced with aqueous alcohol and sodium amalgam, yields a *δ-caprolactone-γ-carboxylic acid*,  $CH_2{<}\begin{array}{l}CH(COOH)\cdot CHMe\\ CH_2{-}{-}{-}{-}{-}{-}{-}CO\end{array}{>}O$; it forms a syrupy mass which, on drying at 120—125° and then cooling, becomes solid, it crystallises in small plates and melts at 107—108°. The acid readily reacts with water; on exposure to moist air, it is converted into a syrup consisting of a mixture of the δ-lactone-monocarboxylic acid and the δ-hydroxydicarboxylic acid. (Compare Weidel, Abstr., 1891, 733.) No salts of the lactonic acid could be obtained, but salts of the hydroxydicarboxylic acid (5-hexanoloic 4-methyloic acid) were easily prepared. The *barium* and *calcium* salts are readily soluble in water, and on evaporation yield a friable mass, whilst the *silver* salt forms a white flocculent precipitate. The acid itself could not be isolated in a state of purity.

When a small quantity of δ-caprolactone-γ-carboxylic acid is distilled, the distillate contains a crystalline dibasic acid, which melts at 152° and is isomeric with the lactonic acid, and a second oily acid which is best separated by distillation in steam. The acid which thus passes over, after purification by means of its barium salt, boils at 206·5°. This *γδ-hexenic acid* is isomeric with hydrosorbic acid, but differs from it in the fact that it becomes crystalline when cooled to – 10° and the crystals then melt at 0°. Its *cadmium* salt is more readily soluble in hot water than in cold and crystallises in large, glistening, flat needles. Cadmium hydrosorbate, on the other hand, is much more sparingly soluble in hot than in cold water. The γδ-hexenic acid is not altered by boiling for 50 hours with a 20 per cent. solution of sodium hydroxide. Hydrosorbic acid when subjected to the same treatment yields αβ-hexenic acid and also β-hydroxycaproic acid (compare Fittig and Baker, Abstr., 1895, i, 206). The author has also reduced benzoylglutaric acid, and then distilled the resulting hydroxy-acid; he finds that the method is a general one for the preparation of γδ-unsaturated acids.

J. J. S.

Thioglyoxylic (Ethanethiolic) Acid. By H. BRUNEL (*Bull. Soc. Chim.*, 1896 [3], 15, 134).—By the action of a solution of sodium carbonate and sodium sulphide on dichloracetic acid, and subsequent treatment of the mixture with sulphuric acid, the author obtains *thioglyoxylic acid*, CHS·COOH, as a viscous substance, decomposing on distillation in a vacuum. It forms unstable lead and silver salts, and, on treatment with alcohol and hydrogen chloride, an *ethylic* salt, boiling at 61° under 36 mm. pressure. On boiling the aqueous solution of the acid with mercuric oxide, glyoxylic acid is produced.

M. W. T.

Transformation of Unsaturated α-Hydroxy Acids into the Isomeric γ-Ketonic Acids. By RUDOLPH FITTIG (*Ber.*, 1896, 29, 2582—2584).—All the substances described by Tiemann and Biedermann (Abstr., 1892, 471) as derivatives of phenylhydroxycrotonic acid have been shown to be derived from benzoylpropionic acid (compare Abstr., 1895, i, 533), which was prepared from succinic anhydride and benzene in the presence of aluminium chloride. The real *α-hydroxy-γ-phenylcrotonic acid*, CHPh:CH·CH(OH)·COOH, can be obtained by saturating a cooled ethereal solution of cinnamaldehyde cyanhydrin with concentrated hydrochloric acid, and then allowing it to remain at the ordinary temperature until no more ammonium chloride separates. It melts at 137°, and also differs in its other properties from benzoylpropionic acid, $COPh·CH_2·CH_2·COOH$;

it is converted almost quantitatively into this acid, however, by boiling with 7 per cent. hydrochloric acid.

Pure crotonaldehyde cyanhydrin behaves in a similar manner although it contains no benzene residue. It yields *α-hydroxypentenoic acid*, $CHMe\!:\!CH{\cdot}CH(OH){\cdot}COOH$, a syrup which takes up 2 atoms of bromine, and yields no phenylhydrazone. Its calcium salt is insoluble in alcohol; when this salt is boiled with excess of dilute hydrochloric acid, levulinic acid, $CMeO{\cdot}CH_2{\cdot}CH_2{\cdot}COOH$, is produced, the calcium salt of which is insoluble in alcohol, and which yields a hydrazone.

It would appear, therefore, that acids of the type

$$R{\cdot}CH\!:\!CH{\cdot}CH(OH){\cdot}COOH$$

are in general transformed into isomeric acids of the type

$$R{\cdot}CO{\cdot}CH_2{\cdot}CH_2{\cdot}COOH$$

when they are boiled with dilute hydrochloric acid. C. F. B.

Volatility of Levulinic Acid. By MARCELLIN BERTHELOT and GUSTAVE ANDRÉ (*Compt. rend.*, 1896, **123**, 341—343).—Levulinic acid is very slightly volatile in steam, but when the dry compound is kept over quicklime or sulphuric acid, it gradually loses weight, the loss being greater in a vacuum than under ordinary pressure, and more rapid over sulphuric acid than over lime. The residue in either case, although crystalline, is partly liquid, and contains less carbon and more hydrogen than the original acid; it would seem that the levulinic acid tends to split up into two parts, the more volatile of which has the composition $4C_5H_8O_3 - H_2O$, whilst the residue seemingly contains dihydroxyvaleric acid. According to this result, levulinic acid is the first anhydride, lactone or olide of the dihydroxyvaleric acid.

C. H. B.

Claisen's Condensation Method. By J. BOËSEKEN (*Rec. Trav. Chim.*, 1896, **15**, 161—164).—The ethereal salts of mono-, di- or trisubstituted acetic acids should react with ethylic acetate in the presence of sodium ethoxide in a manner analogous to the ordinary Claisen condensation. The author has made experiments with the ethylic salts of propionic, phenylacetic, isobutyric, and trimethylacetic acids in the presence of ethylic acetate and sodium ethoxide; but only with ethylic phenylacetate and ethylic propionate did any condensation take place.

The product formed from ethylic acetate and propionate in presence of sodium ethoxide is probably a mixture of ethylic propionylacetate, $CH_2Me{\cdot}CO{\cdot}CH_2{\cdot}COOEt$, and ethylic methylacetoacetate, $COMe{\cdot}CHMe{\cdot}COOEt$, it is a colourless liquid which boils at 192°, and the yield is extremely poor. J. J. S.

Trithiodilactylic Acid. By JOHAN M. LOVÉN (*Zeits. physikal. Chem.*, 1896, **21**, 134—136).—By the interaction of hydrogen sulphide and pyruvic acid, a sulphur compound was obtained which was regarded as trithio-dilactylic acid, this view being supported by its conductivity (Abstr., 1894, 1, 325). The author has further determined the E.M.F. of chains containing the silver salt of the acid, and silver nitrate, and obtained the values 0·157 and 0·171. If the compound contained mercaptan groups, this value should be much higher, so that the previous view of the constitution is confirmed. L. M. J.

Decomposition of Dibromosuccinic Acids with Water. By Wilhelm C. Lossen and Walther Riebensahm (*Annalen*, 1896, **292**, 295—317).—The authors' experiments lead them to the following conclusions.

Dibromosuccinic acids, when treated with 200 parts of boiling water, are decomposed in accordance with the equations

I. $C_4H_4Br_2O_4 = C_4H_3BrO_4 + HBr$.
II. $C_4H_4Br_2O_4 + H_2O = C_2H_4O + 2CO_2 + 2HBr$.
III. $C_4H_4Br_2O_4 + 2H_2O = C_4H_6O_6 + 2HBr$.

The change represented by I affects 50 per cent. of dibromosuccinic acid, only 20 per cent. of dibromisosuccinic acid being decomposed in this manner, more of the latter than of the former undergoing change according to II and III; both acids yield racemic and mesotartaric acids, racemic acid preponderating when dibromisosuccinic acid is used, whilst dibromosuccinic acid yields chiefly mesotartaric acid.

According to the statement of Fresenius, barium racemate separates from boiling solutions in anhydrous crystals, whilst at ordinary summer temperatures the salt contains $2\frac{1}{2}H_2O$. The authors have also obtained a salt containing $5H_2O$ from solutions at ordinary winter temperatures. Barium mesotartrate is usually described as a salt which dissolves readily in hot water, and becomes anhydrous at 100—110°; this, however, is erroneous, as the salt contains $1H_2O$ at 100°, and becomes anhydrous at 170°. M. O. F.

Malononitrile and some of its Derivatives. By B. C. Hesse (*Amer. Chem. J.*, 1896, **18**, 723—751. Compare Abstr., 1896, i, 458).—The malononitrile (m. p. 29°; b. p. 219—220°) used by the author was prepared by distilling dry cyanacetamide with an equal weight of phosphorus pentachloride. It is incidentally shown that dibromocyanacetamide and not the monobromo-derivative is the chief product of the interaction of cyanacetamide and bromine in cold aqueous solution (compare Nef, *Annalen*, 1894, **280**, 334). The action of bromine on the nitrile is complex, but both the monobromo- and dibromo-derivatives were obtained by adding the requisite weight of bromine to an aqueous solution of the nitrile.

Bromomalononitrile, $CHBr(CN)_2$, is a white, crystalline solid; it melts at 65—66°, and is slightly soluble in water and light petroleum, but dissolves readily in the ordinary organic solvents. *Dibromomalononitrile*, $CBr_2(CN)_2$, a white, crystalline substance, melts at 123·5—124°, and is easily soluble in alcohol, ether, and boiling chloroform, but less so in benzene and light petroleum. On pouring a cold aqueous solution of malononitrile (1 mol.) into a cold solution of ammoniacal silver nitrate (2 mols.), a mixture of mono- and di-silver malononitrile was obtained.

Diethylmalononitrile, $CEt_2(CN)_2$, was prepared both by heating a mixture of ethylic iodide (56 grams) and silver malononitrile (25 grams), and also by heating these substances with ether for 5 hours in a sealed tube at 100°. In both cases, the yields were low—15·6 per cent. and 6·4 per cent. of the theoretical quantities respectively, ethylic isocyanide and amorphous substances being formed at the same time. Diethylmalononitrile is a white, crystalline substance, which melts at 44°, and is insoluble in cold water, but soluble in hot water and in the ordinary organic solvents. (Compare next abstract.)

Dimethylmalononitrile, $CMe_2(CN)_2$, prepared similarly, is a white, crystalline solid melting at 32—32·5°, easily soluble in alcohol, ether, acetone and ethylic acetate, less soluble in chloroform, benzene and light petroleum, and insoluble in water. (Compare next abstract.)

The bearing of the formation of dialkylmalononitriles (accompanied by the formation of alkylic isocyanides), as above described, on the constitution of disilver malononitrile, is discussed, and the formula $AgN\colon C\colon C\colon C\colon NAg$ is considered to be most probable. Attempts to prepare disodiomalononitrile by the interaction of sodium and malononitrile in ethereal solution with the addition of small quantities of alcohol, resulted in the formation of a substance which was apparently a mixture of the monosodium compound and sodium ethoxide. It reacts with alkylic iodides (see below) as though it contained both mono- and di-sodio-nitrile, and gave hydrocyanic acid with dilute acids. This fact is regarded as evidence that the metal is in direct combination with nitrogen. When this substance is heated with ethylic or methylic iodide, dimethyl- or diethyl-malononitrile is formed; in both cases hydrocyanic acid is also formed, and this is attributed to the decomposition of the monalkylmalononitrile. When ethylic chloroformate is added to an alcoholic solution of malononitrile containing one equivalent proportion of sodium ethoxide, a reaction occurs at once with formation of Haller's ethylic sodiodicyanacetate (Abstr., 1890, 1395) to the extent of 70 per cent. of the theoretical yield. Another substance yielding a yellowish precipitate with silver nitrate is also produced.

Methylic sodiodicyanacetate, prepared in similar manner, is soluble in ethylic acetate, and is precipitated from its alcoholic solution by benzene, light petroleum, chloroform and ether. When boiled with concentrated sodium hydroxide solution, no ammonia is formed, and it does not react with dilute (1 : 5) sulphuric acid. In its stability towards hydrolysing reagents, it resembles the corresponding ethylic salt.

The action of methylic iodide on a mixture of malononitrile and sodium methoxide in methylic alcohol solution gave, as the chief product, an oil boiling at 74—76° (22 mm.) having a fragrant, mintlike odour. Analysis pointed to the presence of 20 per cent. of dimethylmalononitrile with 80 per cent. of its imido-methyl ether, $CN\cdot CMe_2\cdot C(NH)\cdot OMe$; the existence of the latter was proved by treating the oil with dilute hydrochloric acid, when it underwent decomposition into methylic dimethylcyanacetate and ammonium chloride.

When ethylic alcohol and ethylic iodide were substituted for the corresponding methyl compounds in the above experiment, the products obtained were diethylcyanacetamide and an oil consisting of diethylmalononitrile and its imido-ethyl ether. When this oil was dissolved in absolute ethylic alcohol containing some sodium ethoxide, and allowed to stand for 28 hours, almost the whole of the nitrile was converted into the imido-ether, a colourless mobile oil of mint-like odour; the action of aqueous hydrochloric acid changes this into ethylic diethylcyanacetate, a colourless oil of fragrant odour, boiling at 100—101° (14 mm.).

Diethylcyanacetamide, $CN{\cdot}CEt_2{\cdot}CO{\cdot}NH_2$, is formed in the above reaction, also in the preparation of diethylmalononitrile from the sodium salt and ethylic iodide in sealed tubes, and by boiling diethylmalononitrile with absolute alcohol containing 1·3 per cent. of sodium. In the last reaction, it is probable that the dialkyl amido-ether, $CN{\cdot}CEt_2{\cdot}C(OEt)_2{\cdot}NH_2$, is first formed, and that this at the boiling point of alcohol loses ethylic ether and forms the amide (compare Trans., 1896, 991). This crystallises in colourless plates melting at 120°, and is soluble in alcohol, ether and chloroform; less so in light petroleum and benzene.

Diethylcyanacetic acid, $CN{\cdot}CEt_2{\cdot}COOH$, was prepared (1) from the oil obtained in the reaction between ethylic iodide, malononitrile and sodium ethoxide, (2) from diethylmalononitrile, and (3) by heating diethylcyanacetamide in sealed tubes at 100° for 2 hours with concentrated hydrochloric acid. It was obtained as a colourless oil boiling at 162—164° (18 mm.), but this soon solidified to a white, hygroscopic, ice-like solid melting at 57°. The cyanogen group is very stable, being unaffected by heating with concentrated hydrochloric acid in a sealed tube for 1 hour at 120°. The *silver* salt crystallises from boiling water in glistening needles. On heating with concentrated hydrochloric acid in a sealed tube at 160° for 8 hours, diethylcyanacetic acid is quantitatively converted into diethylacetic acid, a fact which shows that in all those substances yielding diethylcyanacetic acid the two ethyl groups are attached to the same carbon atom. The author is of opinion that in the metallic derivatives of malononitrile the metal is directly linked to nitrogen, and discusses the mechanism of the changes resulting in the production of the dialkyl derivatives and of the monimido ethers. A. C. C.

Malononitrile Derivatives and their Reduction. By Giorgio Errera and E. Bertè (*Gazzetta*, 1896, **26**, ii, 220—228).—The authors have prepared malononitrile derivatives of the constitution $CR_2(CN)_2$ and find them to be very stable substances which are not affected by light as are those having the constitution $CHR(CN)_2$ prepared by Henry (*Jahresber.*, 1889, 637).

Dibenzylmalononitrile, $C(CH_2Ph)_2(CN)_2$, may be prepared by the action of sodium on an alcoholic solution of malononitrile and benzylic chloride, but is best obtained by heating dibenzylcyanacetamide (Errera, Abstr., 1895, i, 528) with phosphoric anhydride at 170—180°; the product is extracted with water, and the residue crystallised from alcohol. It forms long, colourless laminæ melting at 130°, and is soluble in alcohol, but insoluble in water.

Dipropylmalononitrile, $CPr_2(CN)_2$, is prepared by heating dipropylcyanacetamide with phosphoric anhydride, and after extraction with water is crystallised from petroleum; it separates in large, colourless crystals melting at 46—47°, and boils at 223—225°. It is soluble in organic solvents but not in water.

Diethylmalononitrile, $CEt_2(CN)_2$, is prepared in a manner similar to the preceding, and is purified by distillation in a current of steam; it forms a colourless, crystalline mass melting at 44—45°, and boiling at 195—195·5°; its odour slightly resembles that of camphor.

Dimethylmalononitrile, $CMe_2(CN)_2$, resembles the preceding in appearance and odour; it sublimes in long needles melting at 31—32°, and boils at 162·5°. (Compare preceding abstract.)

Dibenzylmalononitrile in alcoholic solution is reduced by sodium; after adding water, acidifying and boiling off the alcohol, ether extracts dibenzylcyanacetamide and dibenzylacetamide from the aqueous solution, and on concentrating the latter, the hydrochloride of *β-dibenzylethylamine*, $CH(CH_2Ph)_2 \cdot CH_2 \cdot NH_2$, is deposited. The free base is a heavy liquid of alliaceous ammoniacal odour, and is insoluble in water; the *hydrochloride* crystallises in long, white needles, melting at 189—190° and is very soluble in alcohol, but only sparingly so in dilute hydrochloric acid. The *platinochloride* crystallises in lustrous yellow laminæ, melting and decomposing at 216—218°.

The subcutaneous injection of 0·30 gram of the hydrochloride is fatal to a rabbit, and on injecting the solution into the eye of a rabbit, local anæsthesia is produced. W. J. P.

Reduction of Dipropylmalononitrile. By GIORGIO ERRERA (*Gazzetta*, 1896, **26**, ii, 244—248. Compare preceding abstract).—Dipropylmalononitrile is reduced by boiling its alcoholic solution with sodium, and, on distilling the product in a current of steam, a solution of 4′-amino-4-methylheptane passes over and dipropylacetamide remains behind.

Dipropylacetamide, $CH(C_3H_7)_2 \cdot CO \cdot NH_2$, crystallises in brilliant, white needles melting at 123—124° and is soluble in alcohol or ether.

4′-*Amino*-4-*methylheptane*, $CH(C_3H_7)_2 \cdot CH_2 \cdot NH_2$, is separated from the distillate obtained as above by evaporating it with hydrochloric acid; after adding potash, the base is extracted with ether. It is a colourless liquid of unpleasant, alliaceous odour, and boils at 167°; it is soluble in alcohol or ether, but only sparingly so in water or alkalis. It gives the isonitrile reaction. The *hydrochloride*, a white, waxy mass, is very soluble in water, alcohol, or ether; the *platinochloride* crystallises in yellow laminæ, melting and decomposing at 211°. The *benzoyl*-derivative, $CHPr_2 \cdot CH_2 \cdot NH \cdot COPh$, prepared by the action of benzoic chloride and potash on the base, crystallises in needles melting at 66—67°, and is very soluble in organic solvents, but insoluble in water. W. J. P.

Syntheses in the Adipic Acid Series. By CLEMENTE MONTEMARTINI (*Gazzetta*, 1896, **26**, ii, 259—290. Compare Abstr., 1896, i, 667).—On treating an alcoholic solution of ethylic malonate with sodium, and heating in a reflux apparatus with ethylic γ-chlorobutyrate

(Gabriel, Abstr., 1890, 1121), then adding water and extracting with ether, an oil is obtained which, by fractional distillation under reduced pressure, can be separated into ethylic malonate, ethylic γ-chlorobutyrate and an *ethylic butanetricarboxylate* having the constitution $CH(COOH)_2 \cdot CH_2 \cdot CH_2 \cdot CH_2 \cdot COOH$. The ethylic salt is a colourless liquid boiling at 175—176° under 18 mm. pressure, and having the sp. gr. 1·0726 at 15°; it is readily hydrolysed by boiling with alcoholic potash, and after driving off the alcohol and acidifying with hydrochloric acid, the *tricarboxylic acid* can be extracted with ether. It crystallises in needles, melting and decomposing at 130°, and is soluble in ethylic acetate, but nearly insoluble in benzene; its *silver* salt, $Ag_3C_7H_7O_6$, forms a white, crystalline precipitate, and its *calcium* salt crystallises with $2H_2O$. When heated at 150°, the acid decomposes, giving adipic acid and carbonic anhydride.

On condensing ethylic methylmalonate and ethylic γ-chlorobutyrate with sodium in a similar manner, the *triethylic* salt, $C_{14}H_{24}O_6$, of a homologous pentanetricarboxylic acid is obtained as a colourless oil boiling at 181—183° under 12 mm. pressure; on hydrolysing the salt with alcoholic potash, the *pentanetricarboxylic acid* is obtained as an uncrystallisable syrup, which begins to lose carbonic anhydride at 105°. When distilled under reduced pressure, it yields a syrupy liquid, which contains a trace of adipic acid and partially crystallises over sulphuric acid. It is a mixture of a solid and a liquid acid, which may be partially separated by repeated crystallisation, and completely by heating with acetic chloride on the water bath, adding benzene and then cautiously extracting with water. On evaporating the benzene solution and taking up the residue with water, αβ-dimethylglutaric acid is obtained, whilst the aqueous solution yields α-methyladipic acid (Trans., 1895, 115).

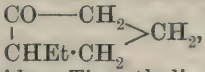
αβ-Dimethylglutaric acid, $COOH \cdot CH_2 \cdot CHMe \cdot CHMe \cdot COOH$, is a liquid which boils at 220—224° under 24 mm. pressure, and yields succinic acid on boiling with chromic acid mixture. It may be synthesised by converting ethylic β-methyllevulinate into the corresponding nitrile by treatment with potassium cyanide and hydrochloric acid, and converting the nitrile into *ethylic α-hydroxy-αβ-dimethylglutarate* by hydrolysis with alcohol and hydrogen chloride: this ethylic salt is an oil which yields αβ-dimethylglutaric acid and glutaric acid on heating it with hydriodic acid. The *silver* salt of dimethylglutaric acid is a white, crystalline precipitate, sparingly soluble in hot water. The acid is converted into a liquid *anhydride* by treatment with acetic chloride, and partially by distillation under reduced pressure; it yields a viscid, uncrystallisable *anilide*, $C_{10}H_{17}NO_3$, when mixed with aniline in benzene solution.

The ethylic butanetricarboxylate, $C_{13}H_{22}O_6$, described above may be methylated by treating it first with sodium ethoxide and then with methylic iodide, whereby the *ethylic* salt,

$$CMe(COOEt)_2CH_2 \cdot CH_2 \cdot CH_2 \cdot COOEt,$$

of a homologous tricarboxylic acid is produced; this is a colourless oil, boiling at 182—185° under 32 mm. pressure, and yields a solid *pentanetricarboxylic acid* when hydrolysed with alcoholic potash. The acid decomposes on distillation, yielding α-methyladipic acid, but no $\alpha\beta$-dimethylglutaric acid.

On condensing ethylic ethylmalonate with ethylic γ-chlorobutyrate, the *ethylic salt*, $\mathrm{CEt(COOEt)_2{\cdot}CH_2{\cdot}CH_2{\cdot}CH_2{\cdot}COOEt}$, of a tricarboxylic acid is obtained; it boils at 205—208° under 35 mm. pressure, and on hydrolysis with alcoholic potash yields a liquid *hexanetricarboxylic acid*. This when distilled in a vacuum gives a mixture of two isomeric acids, which may be separated by treating with acetic chloride; α-ethyladipic acid and α-ethyl-β-methylglutaric acid are thus obtained.

α-Ethyladipic acid, $\mathrm{COOH{\cdot}CHEt{\cdot}CH_2{\cdot}CH_2{\cdot}CH_2{\cdot}COOH}$, boils at 225—226° under 20 mm. pressure, melts at 46—49°, and gives a very soluble *calcium* salt; it yields succinic acid when oxidised with chromic acid mixture, and when distilled in a vacuum with acetic chloride gives an oil which is insoluble in water, is volatile in a current of steam, and has an odour resembling that of mint. It is an *ethylketopentamethylene*,  $\begin{array}{l}\mathrm{CO{-}{-}CH_2}\\ \mid\\ \mathrm{CHEt{\cdot}CH_2}\end{array}\!\!>\mathrm{CH_2}$, and is the product of decomposition of the anhydride. The ethylic salt described above, which boils at 205—208° under 35 mm. pressure, is readily methylated, yielding the *ethylic* salt, $\mathrm{C_{15}H_{16}O_6}$, of a homologous acid; the *acid* obtained by hydrolysing it with alcoholic potash, yields α-ethyladipic acid when distilled under reduced pressure. W. J. P.

Ethylic Isoallylenetricarboxylate. By GUIDO GOLDSCHMIEDT and GUSTAV KNÖPFER (*Monatsh.*, 1896, **17**, 506—514).—Sodium (1 atom) is dissolved in absolute alcohol and added to a mixture of β-dibromacrylic acid (1 mol.) and ethylic malonate (1 mol.) and the whole is allowed to remain in ice during several days; the subsequent addition of water causes the precipitation of an oil, from which crystals of *ethylic isoallylenetricarboxylate*, $\mathrm{COOEt{\cdot}CH{\vdots}C{\vdots}C(COOEt)_2}$, are deposited and are separated by filtration. The salt thus obtained is insoluble in water and in aqueous alkalis, sparingly soluble in ether, light petroleum and benzene, dissolves readily in acetic acid and melts at 107°; it crystallises from ether in colourless monoclinic prisms $a:b:c = 0{\cdot}70:1:?$. $\beta = 70{\cdot}5°$; its behaviour is not that of an acetylene derivative as it yields no precipitate with ammoniacal cuprous chloride, cupric nitrate, or mercuric chloride. A small quantity of the substance was hydrolysed with potash in a vessel connected with a washing bottle and two flasks containing ammoniacal silver nitrate and mercuric chloride respectively, a stream of air being led through the whole apparatus; no precipitate was produced in either of the solutions, and the alkaline residue, after acidification and extraction with ether, yielded a small quantity of a strongly acid syrup. Ethylic isoallylenetricarboxylate is not attacked by bromine, as would be the case were it an acetylene derivative. A. L.

Ethylic Deoxalate. By ANTON STEYRER and WALTHER SENG (*Monatsh.*, 1896, **17**, 613—635).—The authors have investigated ethylic deoxalate which was first obtained by Löwig by the action of sodium on ethylic oxalate. They find that the best yield of the deoxalate is obtained when ethylic oxalate (3 mols.) is treated with sodium (5 atoms), in the form of 1·5 per cent. sodium amalgam, at a temperature between 5° and 20°. The mixture requires to be constantly shaken and kept at 10—15° for about an hour and a half. The product is extracted three times with anhydrous ether and the residue treated with dilute sulphuric acid, and not with water, as suggested by Löwig.

The acidified residue was found to contain oxalic acid and racemic acid, but no sugar (compare Löwig). The ethereal extract, if the above conditions be fulfilled, after evaporating the ether and keeping for several days, sets to a crystalline mass of ethylic deoxalate. If less than 5 atoms of sodium are used to 3 mols. of ethylic oxalate, the residue remains syrupy and contains alcohol, ethylic carbonate, and ethylic oxalate, besides ethylic deoxalate.

The deoxalate is slowly hydrolysed by cold water, more readily by hot, and is best recrystallised from a mixture of alcohol and ether. It may also be purified by distillation under diminished pressure, when it passes over at 156°—157° under a pressure of 2 mm. It forms colourless crystals, melts at 78° (corr.) and dissolves in cold water, yielding a perfectly neutral solution. On treatment with warm ammonia, it gives a yellow solution, which, in contact with the air turns reddish violet. Analyses, and also the estimation of ethyl groups by Zeisel's method, agree with the formula $C_5H_3Et_3O_8$.

The vapour density as determined by Hofmann's method shows that complete dissociation takes place at 180—210°.

Phenylhydrazine reacts with ethylic deoxalate to form the *ethylic* salt of E. Fischer's phenylhydrazineglyoxylic acid. This crystallises from aqueous alcohol in glistening, yellow plates, and melts at 127°. Hydroxylamine, on the other hand, yields glycollic acid and the *oxime of ethylic mesoxalate*—which is identical with Conrad and Bischoff's ethylic isonitrosomalonate (Abstr., 1882, 39). Other substances are probably formed at the same time. J. J. S.

Action of Formaldehyde on Carbamide. By CARL GOLDSCHMIDT (*Ber.*, 1896, **29**, 2438—2439). When formaldehyde is added to a solution of carbamide in dilute hydrochloric acid, a granular precipitate is produced which does not dissolve in any of the usual solvents. This substance is formed by the reaction of 2 molecules of carbamide with 3 of the aldehyde, and has the empirical formula $C_5H_{10}N_4O_3$. It is decomposed by strong acids but is not affected by alkalis. A. H.

Ammoniacal Fermentation of Uric Acid. By FAUSTO SESTINI and LEONE SESTINI (*Gazzetta*, 1896, **26**, ii, 92).—In connection with the recent work of Gérard (*Compt. rend.*, 1896, **122**, 1019), the authors point out that they were the first to study, chemically and bacteriologically, the fermentation of uric acid (Abstr., 1890, 1399). W. J. P.

Action of Alkali Hypobromites on Succinodiamide. By W. VAN DAM (*Rec. Trav. Chim.*, 1896, **15**, 101—106).—The author has obtained succinodibromdiamide, $(CH_2\cdot CO\cdot NHBr)_2$ or

$$CH_2\cdot CO\cdot NBr_2,CH_2\cdot CO\cdot NH_2,$$

by a method slightly different from that given by van Ligne. Finely powdered succinamide was treated with the theoretical quantity of potassium hypobromite solution. The mixture was cooled and constantly stirred until it set to a pasty mass, which was then poured into 10 per cent. acetic acid. The bromamide was collected, well washed with ice-cold water, and then dried over sulphuric acid and potash.

When the succinodibromodiamide is treated with barium hydroxide solution first in the cold and then at 30—40°, it yields β-lactylcarbamide (compare Lengfeld and Stieglitz, Abstr., 1893, i, 632). The same compound can be obtained directly from succinodiamide by the action of a mixture of potassium hypobromite and hydroxide.

J. J. S.

Action of Alkali Hypochlorites and Hypobromites on Amides. By SEBASTIAAN HOOGEWERFF and WILLEM ARNE VAN DORP (*Rec. Trav. Chim.*, 1896, **15**, 107—115).—A historical survey of the work done by the authors and others on the action of alkali hypochlorites and hypobromites on acid amides. Compare Abstr., 1887, 245; 1888, 1194; 1889, 981; 1891, 196, 1216. Lengfeld and Stieglitz (Abstr., 1893, i, 310, 631; 1894, i, 415).

The authors show that part of the work done by Weidel and Roithner (Abstr., 1896, i, 470) has been previously published by themselves.

J. J. S.

Oximamidoxalic Acid and Hydroxyoxamide. By ARNOLD F. HOLLEMAN (*Rec. Trav. Chim.*, 1896, **15**, 148—156).—Schiff and Monsacchi have claimed that the compound described by them (Abstr., 1896, i, 209) as hydroxyoxamide, $NH_2\cdot CO\cdot CO\cdot NH\cdot OH$, is identical with the compound previously described (Abstr., 1894, i, 571) as oximamidoxalic acid, $NH_2\cdot C(NOH)\cdot COOH$.

It is now pointed out that the compounds cannot be identical for the following reasons.

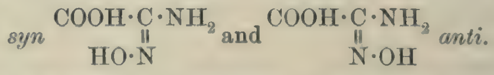
Schiff and Monsacchi's compound is coloured brownish-red by ferric chloride. It yields an acetyl derivative (m. p. 178°), and a benzoyl derivative (m. p. 157°) which easily crystallises.

Holleman's compound is coloured reddish-violet by ferric chloride. When heated with acetic acid and acetic anhydride, it yields no acetyl derivative, but is decomposed yielding cyanamide, but it yields an unstable benzoyl derivative, which is decomposed by hot alcohol.

The author thinks that Schiff and Monsacchi's compound has more the properties of $NH_2\cdot C(NOH)\cdot COOH$ than of $NH_2\cdot CO\cdot CO\cdot NH\cdot OH$; thus it is not readily oxidised, whereas all substituted hydroxylamines are oxidised with the greatest ease. Its acetyl and benzoyl derivatives have fairly strong acid properties. The formula $NH_2\cdot C(NOH)\cdot COOH$

also accounts for the fact that oxalic acid, ammonia and hydroxylamine are obtained when the compound is heated with hydrochloric acid on the water bath.

The author still retains the same constitution for his own substance, and as the possibility of the two substances being polymerides has been proved untenable by molecular weight determinations, they are probably stereoisomeric, as represented by the formulæ



$$\textit{syn}\ \begin{array}{rcl}\mathrm{COOH\cdot}&\mathrm{C}&\mathrm{\cdot NH_2}\\ &\Vert& \\ \mathrm{HO\cdot}&\mathrm{N}& \end{array}\ \text{and}\ \begin{array}{rcl}\mathrm{COOH\cdot}&\mathrm{C}&\mathrm{\cdot NH_2}\\ &\Vert& \\ &\mathrm{N}&\mathrm{\cdot OH}\end{array}\ \textit{anti.}$$

The author gives the syn-formula to his own compound since it more readily accounts for the formation of cyanamide by the action of acetic anhydride (*loc. cit.*). The anti-configuration is given to Schiff and Monsacchi's compound as this more readily accounts for the formation of carbonic anhydride and carbamide when heated.

J. J. S.

Malic Derivatives of Aliphatic Amines. By ARNALDO PIUTTI and ERCOLE GIUSTINIANI. (*Gazzetta*, 1896, **26**, i, 431—440).—Körner and Menozzi (Abstr., 1895, i, 591), having prepared a methylfumaramic acid melting at 208°, by the action of methylic iodide and potash on dimethylasparagine, stated that the substance melting at 149° which Giustiniani obtained (Abstr., 1892, 821) by the action of alkali on the methylfumarimide prepared by distilling methylamine hydrogen malate cannot also be a methylfumaramic acid. The explanation of the disagreement is now given.

On heating ethylic hydrogen fumarate with absolute alcohol and dry methylamine for 3 hours at 110°, ethylic hydrogen methylaspartate is obtained instead of a synthetical methylfumaramic acid.

On mixing a benzene solution of malic anhydride with the equivalent quantity of an absolute alcoholic solution of methylamine, heat is developed and Giustiniani's acid melting at 149° crystallises out; on heating on the water bath with potash until all the methylamine is driven off, and then acidifying with hydrochloric acid, fumaric acid separates, but if the hydrolysis be performed with baryta, and the liquid acidified with sulphuric acid, malic acid is obtained. The acid melting at 149° decomposes above its melting point, yielding the so-called methylfumarimide melting at 90—92°.

It is consequently evident that the acid melting at 149° is *methylmalamic acid* and the imide melting at 90—92° is *methylmalimide.* Similarly, it is shown that Giustiniani's ethylfumaramic and benzylfumaramic acids are really malic derivatives, for when hydrolysed with baryta they yield malic acids; further, the corresponding imides melting at 45·5° and 67·5° must be regarded as ethylmalimide and benzylmalimide respectively.

The three malamic acids have the normal molecular weights by the ebullioscopic or cryoscopic method.

W. J. P.

Coal tar Thioxen [Dimethylthiophen]. By KARL KEISER (*Ber.*, 1896, **29**, 2560—2564).—Experiments were made with the view of ascertaining whether the dimethylthiophen of coal tar is, like coal tar xylene, a mixture of different isomerides.

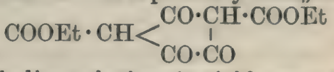
For this purpose, the crude oil was treated with bromine and the product distilled in a current of steam, when the xylenes first passed over, being followed by the bromo-compound, which sank to the bottom of the receiver. By subsequently fractionating this, *bromodimethylthiophen*, C_4SHMe_2Br, was obtained as a heavy, colourless oil boiling at 204—207°. On sulphonating this compound by Tohl's method, eliminating the bromine with sodium amalgam, converting the sulphonic acid into the chloride, and treating this with excess of ammonium carbonate, the mixed dimethylthiophensulphonamides, $C_4SHMe_2\cdot SO_2\cdot NH_2$, were obtained. From this, by fractional recrystallisation, the following compounds were isolated: (1) Fine needles, melting at 264°; (2) white, glistening needles, melting at 258°; (3) glistening prisms, melting at 225°; and (4) small needles, melting at 135°. The last compound was found to be identical with the sulphonamide of synthetically prepared 2 : 5 dimethylthiophen.

J. F. T.

Action of Aluminium Chloride on Benzene containing Thiophen. By Eyvind Boedtker (*Compt. rend.*, 1896, **123**, 310—311).—When ordinary crystallisable benzene is boiled with aluminium chloride, hydrogen sulphide is liberated, and the thiophen is decomposed, one of the products being a brown liquid with a green fluorescence; this boils above 300°, and contains traces of sulphur, but does not give the thiophen reaction. It is probable that the thiophen residue after elimination of sulphur combines with the residues of 2 molecules of benzene from which hydrogen has been eliminated. A condensed thiophen may be formed at the same time, as Hauer has supposed.

C. H. B.

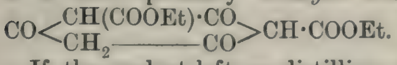
Synthesis of Homocyclic Compounds. By Enrico Rimini (*Gazzetta*, 1896, **26**, ii, 325—380).—Ethylic acetonedicarboxylate and ethylic oxalate readily condense when dissolved in sodium ethoxide solution; when the insoluble sodium salt deposited is washed with ether and acidified, a substance which crystallises in small, white needles decomposing at 140—156° is obtained. It is probably *diethylic triketopentamethylene*-1:3-*dicarboxylate*,



$$\mathrm{COOEt\cdot CH}\Big<\begin{array}{l}\mathrm{CO\cdot CH\cdot COOEt}\\ \qquad\quad|\\ \mathrm{CO\cdot CO}\end{array};$$

when treated with hydroxylamine in alkaline solution, it yields, not a trioxime, but a *substance* of the composition $C_9H_{13}NO_9$.

On heating diethylic acetonedicarboxylate with ethylic malonate and sodium ethoxide, condensation occurs, and a substance is obtained which crystallises in beautiful, yellow pyramids melting at 100—101°; it is most probably *diethylic triketohexamethylene*-1:3-*dicarboxylate*,



$$\mathrm{CO}\Big<\begin{array}{l}\mathrm{CH(COOEt)\cdot CO}\\ \mathrm{CH_2}\text{———}\mathrm{CO}\end{array}\Big>\mathrm{CH\cdot COOEt}.$$

If the product left on distilling off the solvent from an alcoholic solution of ethylic acetonedicarboxylate, ethylic succinate and sodium ethoxide, is suitably treated, it yields ethylic succinylsuccinate, a white, crystalline *substance* of the composition $C_8H_{10}O_4$, which melts at 98°, and an *acid*, $C_7H_6O_4$, which is obtained as a red powder melting at 186—187°. W. J. P.

Action of an Alkali Sulphite on Metadinitrobenzene. By RUDOLF NIETZKI and G. HELBACH (*Ber.*, 1896, **29**, 2448—2450).—When metadinitrobenzene is heated with sodium sulphite solution, it is converted into *nitranilinesulphonic acid* [$NH_2 : NO_2 : SO_3H = 4 : 2 : 1$] which is very sparingly soluble in hot water, and crystallises in almost colourless, microscopic needles. Dilute sulphuric acid at 180° converts it into metanitraniline and sulphuric acid. The *potassium salt* crystallises in yellow quadratic plates. Nitrous acid converts the acid into an almost insoluble diazo-salt, and this, on boiling with alcohol yields a nitrosulphonic acid, which is converted by reduction into orthoanilinesulphonic acid. Since the nitranilinesulphonic acid is identical with that obtained by the reduction of dinitrobenzenesulphonic acid [$(NO_2)_2 : SO_3H = 4 : 2 : 1$], it follows that it has the constitution assigned to it above. It is not, however, identical with the acid which was obtained by Pohl and Hartung (*Annalen*, **205**, 102) by the direct sulphonation of metanitraniline. On reduction, the metanitranilinesulphonic acid is converted into *metaphenylenediaminesulphonic acid*, which crystallises in colourless rhombic tablets and is converted by nitrous acid into a colouring matter of the phenylene-brown series. The corresponding *nitrohydrazinesulphonic acid* and its *hydrochloride* have also been prepared as well as 3-*nitrophenol*-4-*sulphonic acid*, the *potassium salt* of which crystallises in yellow plates. A. H.

Preparation of Phenylacetylene. By ARNOLD F. HOLLEMAN (*Rec. Trav. Chim.*, 1896, **15**, 157—158. Compare Abstr., 1888, 261).—Phenylacetylene is best obtained by gently distilling phenylpropiolic acid with an excess of aniline, and pouring the distillate into dilute hydrochloric acid, when the phenylacetylene separates in an oily form, and may be extracted with ether; the yield is extremely good.

J. J. S.

Solid Solutions of Phenol in Benzene. By FELICE GARELLI (*Gazzetta*, 1896, **26**, ii, 107—119).—The author has previously observed that phenol depresses the freezing point of benzene anomalously (Abstr., 1894, i, 157); in order to determine whether this is due to the formation of a solid solution of phenol in the freezing benzene, test experiments were made by Küster's method. Phenol and benzil were dissolved together in benzene, and the solution cooled as in molecular weight determinations by the cryoscopic method; the solid deposited was then separated and analysed. The quantity of phenol found in the frozen benzene was always greater than that of the benzil, so that the anomalous depression of the freezing point of benzene by phenol may be attributed to the formation of a solid solution of phenol in benzene; as the benzene solution is made more concentrated, the percentage of phenol in the solid which separates decreases continuously with the increase of the concentration, and this the author believes to be due to the fact that such solutions congeal at a lower temperature, This point is of interest in connection with the distribution of a dissolved substance between two solvents in contact; if the phenol has the same molecular weight both in the liquid and solid benzene solution, the distribution of the phenol between the two kinds of solution should be independent of the concentration. Experiment shows, however, that the coefficient of distribution is much affected by change of temperature, and if benzene solutions of phenol be caused to freeze at a lower temperature by the addition of benzil, the proportion of the total phenol found in the solid solution is less than it would otherwise be. W. J. P.

Action of Sodium Sulphide on 1:4-Chloronitrobenzene. By FRIEDRICH KEHRMANN and EDUARD BAUER (*Ber.*, 1896, **29**, 2362—2367).—When the solution obtained by treating 1:4-chloronitrobenzene (1 mol.) with a cold alcoholic solution of sodium sulphide (1·5 mol.) is poured into water, the sodium salt of nitrothiophenol remains in solution, whilst a yellow, crystalline mass separates. Boiling dilute hydrochloric acid extracts *nitramidophenylic sulphide* from the solid mixture. It can be precipitated by ammonia and recrystallised from benzene, when it forms extremely long, orange-coloured prisms with a bluish glance. It melts at 143°, is insoluble in water, but is readily soluble in all organic solvents, and has the constitution

$$NO_2\cdot C_6H_4\cdot S\cdot C_6H_4\cdot NH_2\,[4:1:4].$$

Its *hydrochloride* crystallises in glistening, white needles, which are decomposed by water. On treatment with acetic anhydride, the base is converted into an *acetyl* derivative, which melts at 193°; and on reduction with stannous chloride, it yields Merz and Weith's thioaniline, which Nietzki and Bothof (Abstr., 1895, i, 132), have shown to be paradiamidophenylic sulphide.

An alcoholic solution of the nitroamido-compound on treatment with concentrated sodium nitrite solution yields *paranitrophenylic sulphide*, $Ph\cdot S\cdot C_6H_4\cdot NO_2$, which crystallises in pale yellow, transparent prisms and melts at 55°. On reduction with stannous chloride this nitro-compound yields *paramidophenylic sulphide* which melts at 93°; its *acetyl* derivative melting at 146°. Nietzki and Bothof's paradinitrophenylic sulphide (*loc. cit.*) on reduction with ammonium sulphide gives the above-mentioned nitroamino-base.

The residue left on extracting the yellow, crystalline mass with dilute hydrochloric acid yields, after several crystallisations from benzene, *paradichlorazoxybenzene*, which crystallises in colourless prisms and melts at 155° (compare Laubenheimer, *Ber.*, **8**, 1626).

If a larger quantity of sodium sulphide (2 mols.) is used, the chief products are, besides nitrothiophenol, thioaniline, parachloraniline, and the azoxy-compound. J. J. S.

Migration of an Iodine Atom in Anisoïl and Phenetoïl Derivatives. II. By FRÉDÉRIC REVERDIN (*Ber.*, 1896, **29**, 2595—2599. Compare Abstr., 1896, i, 475).—Red 4:3-*iodonitranisoïl*, melting at 62°, was prepared by the action of potassium iodide on the diazo-compound from 3:4-nitranisidine; this amine was obtained by hydrolysing 3 : 4-*nitracetanisidide*, a yellow substance, melting at 117°, which is formed when 4-acetanisidide is boiled with 11 per cent. nitric acid.

Derivatives of phenetoïl were also experimented with; they were prepared in the same way as the analogous anisoïl derivatives already examined. 2-*Iodophenetoïl* boils at 245° under 735·5 mm. pressure, and yields yellow 2 : 4-*iodonitrophenetoïl*, melting at 96°. This can be reduced to 2 : 4-*iodophenetidine*, the yellow *picrate* of which begins to decompose at 180°, whilst the *thiocarbamide, acetylderivative*, and condensation product with 1 : 2 : 4-chlorodinitrobenzene melt at 163°, 146°, and 172° respectively; the base itself, by means of the diazoreaction, can be made to yield 2 : 4-*diiodophenetoïl*, which melts at 51°. 4-*Iodophenetoïl* melts at 29°, and boils at 249—250° under 729 mm. pressure; when nitrated, it yields the 2 : 4-iodonitro-compound mentioned above, the iodine atom having migrated to the 2 position.

4-Brom- and 4-chlor-anisoïl behave normally when nitrated, yielding compounds isomeric, and not identical, with those obtained by the nitration of 2-brom- and 2-chlor-anisoïl; no migration of the iodine atom takes place. 4-*Chloro-2-nitranisoïl* is apparently described for the first time; it is yellowish, and melts at 98·5°.

C. F. B.

Xylenolbromethylic Ether. By GEORG M. J. SCHRADER (*Ber.*, 1896, **29**, 2399—2403).—*a-Metaxylylic bromethylic ether*,

$$C_6H_3Me_2{\cdot}O{\cdot}CH_2{\cdot}CH_2Br,$$

$[Me_2 : O = 1 : 3 : 4]$ is formed when ethylene bromide is boiled with an alcoholic solution of sodium ethoxide and 1 : 3 : 4-xylenol, and is a slightly brownish oil, which boils at 263—265°. It readily reacts with potassium phthalimide to form 1 : 3 : 4-*xylenoxyethylphthalimide*, $C_6H_3Me_2{\cdot}O{\cdot}CH_2{\cdot}CH_2{\cdot}N{:}(CO)_2{:}C_6H_4$, which crystallises in long, yellowish-white needles, melting at 113—114°. This compound cannot be directly used for the preparation of xylenoxyethylamine since the latter is decomposed by hydrochloric acid at the temperature required for the hydrolysis. It is therefore converted into 1 : 3 : 4-*xylenoxyethylphthalamic acid*, $C_6H_3Me_2{\cdot}O{\cdot}C_2H_4{\cdot}NH{\cdot}C_6H_4{\cdot}COOH$, which crystallises in fascicular groups of needles, melting at 130—131°. When this is heated with hydrochloric acid on the water bath, it yields 1 : 3 : 4-*xylenoxyethylamine hydrochloride*, as a yellowish-white mass which has not been obtained pure. The free *base* is a strongly alkaline liquid, which boils at 249—250°. The *picrate* melts at 182—183°, and the *platinochloride* melts and decomposes at 211°. 1 : 3 : 4-*Xylenoxyethylbenzamide*, $C_{10}H_{13}O{\cdot}NHBz$, crystallises in slender needles, melting at 117—118°. *a-Metaxylenoxyethylacetamide* forms long, white needles, melting at 70—71°. *a-Metaxylenoxyethylcarbamide* crystallises in plates and melts at 132—133°. 1 : 3 : 4-Xylylic bromethylic ether is converted by aniline into 1 : 3 : 4-*xylenoxyethylaniline*,

$$C_6H_3Me_2{\cdot}O{\cdot}C_2H_4{\cdot}NHPh;$$

this is an oily basic liquid, the *hydrochloride* of which crystallises in colourless plates and melts at 183—184°. Ammonia converts the ether into 1 : 3 : 4-xylenoxyethylamine. Alcoholic potash reacts with the ether to form 1 : 3 : 4-*xylenoxyethylic ether*, $C_8H_9 \cdot O \cdot C_2H_4 \cdot OEt$, which boils at 250—253°. Sodium ethoxide converts the brom-ether into 1 : 3 : 4-*xylylic methylic ethylenic ether*, boiling at 245—247°, whilst sodium phenoxide forms the corresponding *phenylic* 1 : 3 : 4-*xylylic ethylenic ether*, which crystallises in flat prisms, melting at 76—77°. Potassium cyanide acts on the brom-ether as an alkali, yielding as final product *di*-1 : 3 : 4-*xylylic ethylenic ether*, $C_2H_4(O \cdot C_8H_9)_2$, the reaction being similar to that which it undergoes with cresol bromethylic ether. A. H.

Derivatives of Trichlorodinitrobenzene. By C. Loring Jackson and W. R. Lamar (*Amer. Chem. J.*, 1896, **18**, 664—685. Compare Abstr., 1891, 1024).—Trichlorodinitrobenzene (m. p. 129·5°, Abstr., 1887, 136) was prepared by nitrating 1 : 3 : 5-trichlorobenzene which is obtainable in quantity, through the diazo-reaction, from 2 : 4 : 6-trichloraniline prepared according to the directions of V. Meyer and Sudborough (*Ber.*, 1894, **27**, 3151). When heated with aniline, it yields trianilidodinitrobenzene (Abstr., 1890, 247).

5-*Chlorodinitroresorcinol diethyl ether*, $C_6HCl(OEt)_2(NO_2)_2$, is formed by adding an alcoholic solution of sodium ethoxide to a solution of 1 : 3 : 5 : 2 : 4-trichlorodinitrobenzene in a mixture of benzene and alcohol. It crystallises in yellowish-white prisms with square ends, melts at 160°, and dissolves in acetone, benzene, and chloroform, but only slightly in other solvents. When the reaction between sodium ethoxide and trichlordinitrobenzene is allowed to proceed at a higher temperature than that to which the heat of the reaction raises the solvents, *dinitrophloroglucinol triethyl ether*, $C_6H(OEt)_3(NO_2)_2$, is obtained; this crystallises in yellowish prisms terminated at each end by two planes at an obtuse angle to each other, melts at 104—105° and dissolves in hot alcohol or benzene, glacial acetic acid, chloroform and ether, but only sparingly in carbon bisulphide, and not at all in light petroleum and water; it becomes brown on exposure to the air. *Dinitrophloroglucinol diethyl ether*, $C_6H(OEt)_2(NO_2)_2 \cdot OH$, is formed together with the triethyl ether, and is separated from it by treating the product of the reaction with water, when the sodium salt of the diethyl ether dissolves; it crystallises in yellowish-white needles, melts at 166°, and sublimes; most solvents dissolve it, with the exception of light petroleum and cold water. The *sodium* salt dissolves in water, forming a dark orange-red, neutral solution which, when concentrated, yields a bright yellow, gelatinous precipitate with salts of calcium, strontium and barium, salmon-coloured flocks with ferric chloride and yellow flocks with lead acetate and with mercuric chloride.

Ethylic 3 : 5-*dichlorodinitrophenylmalonate*,

$$C_6H(NO_2)_2Cl_2 \cdot CH(COOEt)_2,$$

is prepared by mixing a solution of trichlorodinitrobenzene (1 mol.) in benzene with one of ethylic sodiomalonate (3 mols.) in alcohol, leaving the mixture at the ordinary temperature for 20 hours, and then pouring it into dilute sulphuric acid; the separated benzene is mixed with hot alcohol, when the new compound separates as the solvent cools.

It crystallises in white, thick, narrow plates terminated by two planes at an acute angle to each other; it melts at 101°, and is dissolved by most solvents except water. The *nitrite*,

$$C_6H(NO_2)_2Cl_2\cdot C(NO_2)(COOEt)_2$$

(compare Abstr., 1892, 1217), is formed when the ethylic salt is heated on the water bath with nitric acid (sp. gr. 1·38) for 5 minutes; it crystallises in white crystals, has no definite melting point, and dissolves in most solvents other than light petroleum and water.

3 : 5-*Dichlorodinitrophenylacetic acid*, $C_6H(NO_2)_2Cl_2\cdot CH_2\cdot COOH$, is prepared by boiling ethylic dichlorodinitrophenylmalonate with sulphuric acid (sp. gr. 1·44) in a reflux apparatus. It crystallises in yellowish-white needles, melts at 140°, and dissolves in glacial acetic acid, acetone, benzene, chloroform, ether, and in water containing sulphuric acid, but not in carbon bisulphide or light petroleum; in aqueous soda, it dissolves with a transitory crimson colour (for similar colour changes compare Abstr., 1896, i, 147, 214). The *sodium* salt forms pale yellow crystals; its aqueous solution is neutral, and gives a white flocculent precipitate with ferric chloride, a greenish-blue precipitate with cupric sulphate, a white, curdy precipitate with lead acetate, and a bluish-white precipitate with silver nitrate. The *ethylic* salt is easily obtained by boiling the acid with alcohol, evaporating, extracting with hot dilute sulphuric acid, and crystallising the residue first from light petroleum and then from alcohol. It crystallises in long, white needles, melts at 67—68°, and dissolves best in alcohol and hot light petroleum.

A. G. B.

Derivatives of Veratrole. By AUSONIO DE GASPARI (*Gazzetta*, 1896, **26**, ii, 230—236).—*Monobromoveratrole*, $C_6H_3Br(OMe)_2$, may be prepared by aspirating air containing bromine vapour through a cooled acetic acid solution of veratrole; it is a colourless, highly refractive oil of pleasant odour boiling at 254·5—256° (compare Brüggemann, Abstr., 1896, i, 356). It is readily nitrated by dilute or fuming nitric acid, giving a *bromonitroveratrole*, $C_6H_2Br(OMe)_2\cdot NO_2$, which crystallises in yellow needles melting at 124·5—125°; it is volatile in a current of steam and may be sublimed, but partially decomposes with deflagration. *Bromodinitroveratrole*,

$$C_6HBr(OMe)_2(NO_2)_2,$$

is obtained by treating bromoveratrole with a mixture of sulphuric and fuming nitric acids; it is volatile in a current of steam, and crystallises in yellow needles melting at 113—114°. No trinitro-derivative could be prepared.

A *veratrolesulphonic acid*, $C_6H_3(OMe)_2\cdot HSO_3$, is obtained on heating a solution of veratrole in concentrated sulphuric acid on the water bath; the *barium* salt crystallises with $3H_2O$ in orthorhombic laminæ, loses its water of crystallisation at 140°, and begins to decompose at 145°. The *lead* salt crystallises with $3H_2O$ in pearly orthorhombic laminæ, and is very soluble in water; it becomes anhydrous at 135°. The free acid is volatile in a current of steam, crystallises with $2H_2O$ in laminæ or needles, decomposes at 100° without melting, and effervesces in a vacuum.

On heating the anhydrous sodium or barium salt with phosphorus pentachloride, an oily *sulphochloride* is obtained, which, when treated with ammonia, yields *veratrolesulphonamide*, $C_6H_3(OMe)_2{\cdot}SO_2{\cdot}NH_2$; this crystallises with $2H_2O$ in colourless needles, melting at 136·5—137·5°, and is very soluble in water. The *sulphonanilide*,

$$C_6H_3(OMe)_2{\cdot}SO_2{\cdot}NHPh,$$

crystallises with $2H_2O$ in long, white needles, melting at 130·5—131·5°; the sulphonamide yields an *acetyl*-derivative, $C_6H_3(OMe)_2{\cdot}SO_2{\cdot}NHAc$, which crystallises in thin needles melting at 140—141°.

W. J. P.

Cholesterol, IV. By Julius Mauthner and Wilhelm Suida (*Monatsh.*, 1896, **17**, 579—603).—20 grams of dry cholesterol is dissolved in 1—1·5 litres of glacial acetic acid, and the solution quickly poured into a warm solution of 21 grams of chromic anhydride in ½—1 litre of acetic acid. After pouring into dilute sodium chloride solution, the mass is extracted with ether and the ethereal solution freed from acid substances by shaking with potash. On evaporating the ether, a honey-like mass is left, which gradually deposits a mass of crystals, consisting of three substances; two of these were removed by benzene, and the third—oxycholestendiol—remained behind. The benzene solution was evaporated and the residue fractionally crystallised, first from a small quantity of absolute alcohol, when oxycholestenone separated out in large glistening plates, and finally from dilute alcohol when α-oxycholestenol was obtained.

α-oxycholestenol, $C_{27}H_{42}O_2$, crystallises in colourless needles, melts at 180°, and is readily soluble in all organic solvents. It does not give the typical cholestol reaction, and does not react with phenylhydrazine. It apparently contains one hydroxyl group, as it yields a *monacetyl*-derivative which melts at 101—102°. On careful oxidation, α-oxycholestenol loses 2 atoms of hydrogen, and yields *oxycholestenone*, $C_{27}H_{40}O_2$; this is the chief product obtained on oxidising cholesterol in the manner mentioned above. It crystallises in large, colourless plates, and melts at 122—123°. It contains a carbonyl group, as it readily yields a *phenylhydrazone*, which crystallises in golden yellow, star-shaped crystals, melts at 271°, and gives a characteristic violet-red coloration when dissolved in concentrated sulphuric acid. It apparently contains no hydroxyl group, and does not give the typical cholestol reaction. On treatment with bromine in carbon bisulphide solution, it yields a *dibromo*-derivative, which melts at 167—168°, but it is uncertain whether this is an additive or a substitution product. The dibromo-derivative yields no hydrazone. Oxycholestenone, on further oxidation with an acetic acid solution of chromic anhydride, yields an acid whose *copper* salt has the composition $C_{27}H_{40}CuO_5$.

Oxycholestendiol, $C_{27}H_{42}O_3$, which is insoluble in cold benzene, crystallises from hot absolute alcohol in the form of minute, colourless prisms, melts at 231°, and is much more sparingly soluble than the compounds previously mentioned. It is insoluble in both cold and hot aqueous potash, does not give the characteristic cholestol reaction, and yields no phenylhydrazone. On treatment with alcoholic potash, sulphuric acid, or hydrochloric acid, it is converted into oxycholestenone, and another substance which is being further investigated. Although it does not yield an acetyl-derivative, it seems probable that oxycholestendiol is an α-glycol.

Cholesterol, when more vigorously oxidised (with 24 atoms of oxygen instead of 6), yields a neutral substance, $C_{27}H_{40}O_5$, which melts at 171°, crystallises from alcohol, and does not yield a phenylhydrazone.

Cholesterylic acetate (1 mol.) is slowly oxidised when heated on the water bath with an acetic acid solution of chromic anhydride (6 atoms oxygen). Two compounds are thus formed which are best separated by 75 per cent. methylic alcohol.

β-oxycholestenol acetate, $C_{27}H_{41}O_2Ac$, which is only sparingly soluble in methylic alcohol, crystallises in four-cornered plates and melts at 152—153°. It does not combine with bromine, and does not form a phenylhydrazone. On hydrolysis with sodium methoxide, it yields *β-oxycholestenol*, which is isomeric with the α-compound described above; this crystallises in slender needles, melts at 157°, and does not combine with bromine. When the β-acetate is hydrolysed with alcoholic potash, the elements of water are also eliminated and *oxycholesterylen*, $C_{27}H_{40}O$, is obtained; this crystallises in colourless plates, melts at 112°, and yields a *dibromide* which decomposes at 91—92°. The other neutral product obtained on the oxidation of cholesterylic acetate crystallises from methylic alcohol (75 per cent.) in slender needles and is either $C_{29}H_{44}O_4$ or $C_{29}H_{46}O_4$. On hydrolysis, it yields a compound $C_{27}H_{42}O_3$ or $C_{27}H_{44}O_3$, which melts at 217—218°. Cholesterylic chloride, on oxidation, yields *oxychlorcholesten*, $C_{27}H_{41}ClO$, which crystallises in needles, melts at 121—122°, and does not combine with bromine.

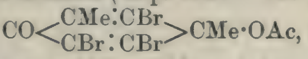
The authors are at present investigating the acid products formed on the oxidation of cholesterol and its derivatives. J. J. S.

Flavone Derivatives, III. By PAUL FRIEDLÄNDER and R. LÖWY (*Ber.*, 1896, **29**, 2430—2435. Compare Abstr., 1896, i, 439).—In reply to the criticism of Kesselkaul and Kostanecki (Abstr., 1896, i, 606), the authors point out that the constitution of the compounds described by them as flavone derivatives rests on the same basis as that of chrysin, since the synthetical flavone derivatives, like this substance, yield acetophenone when heated with caustic soda.

The derivatives described below are obtained by acting with concentrated aqueous potash on a solution of chlorogallacetophenone and the aromatic aldehyde in water or dilute alcohol.

Dihydroxyflavone, prepared from benzaldehyde, has not yet been obtained pure. The *barium salt* crystallises in dark violet needles. The *dibenzoate* forms short, colourless needles, melting at 192·5—194°. The *monomethylic ether* crystallises in pale yellow needles, melts at 158°, and forms a yellowish-brown solution in aqueous soda. The neutral *dimethylic ether* also forms pale yellow needles, and melts at 148—149·5°. The *trihydroxyflavone* prepared from salicylaldehyde crystallises in yellow needles, melting at 214—216°. The *triacetate* forms white, silky needles, melting at 160°. The isomeric *compound* from metahydroxybenzaldehyde melts at 221—223°, and forms a *triacetate*, which melts at 166—167°. The *tribenzoate* melts at 173°. The third *isomeride*, from parahydroxybenzaldehyde, melts at 220°, and its *triacetate* at 199—201°. The *compound* obtained from metanitrobenzaldehyde crystallises well in reddish-yellow needles, and melts at 219—221°; the *acetate* melts at 218—219°. The *compound* formed from dimethylparamidobenzaldehyde crystallises in very sparingly soluble, lustrous, dark red tablets, melting at 203°, which dissolve both in acids and alkalis. The *acetate* forms silky, light red needles, and melts at 182°. Dichlorobenzaldehyde yields a *derivative* which crystallises in yellow needles, and melts and decomposes at 210°. The *acetate* is colourless, and melts and decomposes at 189—191°. The *condensation product* obtained from piperonal crystallises extremely well in reddish-yellow needles, which are very sparingly soluble in the usual solvents and melt at 221°; it forms a magenta-coloured solution in concentrated sulphuric acid. The *diacetate* forms needles which have a distinct yellow colour. The *dibenzoate* melts at 178°, and also forms yellow needles. The *compound* obtained from furfuraldehyde closely resembles the derivatives of the aromatic aldehydes; it crystallises in yellow needles, melting at 224—225°, and yields a *diacetate* which forms silky, pale yellow needles, melting at 201°. A. H.

Keto-Bromides from Asymmetrical Metaxylenol. By Karl Auwers and E. Ziegler (*Ber.*, 1896, **29**, 2348—2355. Compare Abstr., 1896, i, 424).—An ethereal solution of tribromo-xylenol bromide (m. p. 135—136°), when reduced with zinc and hydrobromic acid, yields Jacobsen's tribromometaxylenol (Abstr., 1878, 410). The same compound when treated in acetone solution with water, yields 2 : 3 : 6-*tribromo*-4-*hydroxy*-5-*methylbenzylic alcohol.* This crystallises in glistening needles, melts at 174—176°, is readily soluble in alcohol, ether, acetone, chloroform, &c., but only sparingly in cold benzene and in light petroleum. It is also readily soluble in hot water containing bases in solution. On oxidation, it yields tribromotoluquinone (compare Canzoneri and Spica, Abstr., 1883, 330), and on treatment with methylic alcohol at 100° it is transformed into the methyl ether which has been previously described. This ether, when treated with hydrogen bromide in ice-cold methylic alcohol, is converted into tribromo-xylenol bromide (m. p. 134·5—136°).



"*Tribromo-xylenol acetate,*" $CO<\begin{matrix}CMe:CBr\\CBr:CBr\end{matrix}>CMe\cdot OAc$, crystallises in flat, glistening needles, melts at 153—154°, and is soluble in most organic solvents, but insoluble in water and in alkalis. The *iodide*, obtained from the acetate by means of hydrogen iodide, melts at 134·5—135·5°.

Tribromo-xylenol bromide readily condenses with dimethylaniline to form the *additive compound* $OH\cdot C_6Br_3Me\cdot CH_2\cdot NMe_2PhBr$, which crystallises in white needles, and melts at 225—226° or 231—233°, according to the rapidity with which it is heated. It is converted, by the action of alkalis, into the *free base*, $OH\cdot C_6Br_3Me\cdot CH:NMe_2Ph$, which melts at 121—122°. Like the corresponding pseudocumene derivative, it readily unites with a molecule of methylic iodide; the *methiodide* thus obtained melts at 154° and is decomposed by boiling water.

A condensation product, $OH{\cdot}C_6Br_3Me{\cdot}CH_2{\cdot}C_9NH_7Br$, is obtained by the action of quinoline on tribromo-xylenol bromide. This melts at 232°, and is sparingly soluble in most organic solvents. It is readily soluble in alkalis, and is precipitated unaltered on the addition of an acid.

Piperidotribromo-xylenol, $OH{\cdot}C_6Br_3Me{\cdot}CH_2{\cdot}C_5NH_{10}$, crystallises in small, glistening plates, melts at 155°, is readily soluble in most organic solvents, and is not altered by boiling with alkaline solutions. The pentabromo-derivative, tribromo-xylenol dibromide (Abstr., 1896, i, 424), when reduced with zinc and hydrobromic acid, yields the tribromo xylenol which melts at 179°, and when treated with sodium acetate and acetic acid, yields a *diacetate* which crystallises in flat needles, melts at 172—173°, and is readily soluble in most organic solvents. The diacetate, on treatment with hydrogen chloride in acetic acid solution, yields a *dichloride* which melts between 140° and 150°.

J. J. S.

Constitution of Dibromopseudocumenol Bromide and of its Derivatives. By KARL AUWERS and FRIEDR. BAUM (*Ber.*, 1896, **29**, 2329—2348. Compare Abstr., 1896, i, 149, 150, 420, 421, 423).—The dibromhydroxy-ψ-cumenol previously described (Abstr., 1896, i, 151) is shown to be a *dibromoparahydroxyparaxylobenzylic alcohol* [3 : 6-*dibromo*-4-*hydroxy*-2 : 5-*dimethylbenzylic alcohol*]. It is best prepared by the action of water on a boiling acetone solution of the dibromo-ψ-cumenol bromide. On treatment with acetic anhydride, it yields a monacetate which is insoluble in alkalis.

3 : 6-*Dibromo*-4-*methoxy*-2 : 5-*dimethylbenzylic alcohol* is obtained by treating the hydroxy-alcohol with sodium (1 mol.) and methylic iodide (slight excess) at 100° for 2—3 hours. It crystallises in slender needles, melts at 144°, is insoluble in alkalis, but readily soluble in most organic solvents. It reacts with phenylic cyanate at 100° to form the *urethane*, $OMe{\cdot}C_6H_2Me_2{\cdot}CH_2{\cdot}O{\cdot}CO{\cdot}NHPh$, which crystallises in long, colourless prisms, and melts at 157—158°.

The compounds previously described (Abstr., 1896, i, 150) as methoxy- and ethoxy-dibromopseudocumenol are really the alcoholic ethers of hydroxybenzylic alcohol. As such they readily react with methylic iodide and alkali to form 3 : 6-*dibromo*-4-*methoxy*-2 : 5-*dimethylbenzylic methylic ether*, $OMe{\cdot}C_6Br_2Me_2{\cdot}CH_2{\cdot}OMe$ (m. p. 102—103°), and the corresponding *ethoxy*-compound, $OEt{\cdot}C_6Br_2Me_2{\cdot}CH_2{\cdot}OMe$ (m. p. 98°). The latter is isomeric with 3 : 6-*dibromo*-4-*methoxy*-2 : 5-*dimethylbenzylic ethylic ether*, which melts at 39—40°. On boiling the hydroxy-alcohol with methylic or ethylic alcohol, it is gradually converted into its methyl (91—92°) or ethyl ether (85—87°). On passing hydrogen chloride into a methyl alcoholic solution of the hydroxy-alcohol, the only product formed is dibromo-ψ-cumenol chloride (m. p. 110—111°) (compare Abstr., 1896, i, 423), hydrogen bromide yields the corresponding bromide. The alcoholic ethers yield the same products when treated in a similar manner; the dimethylic ether, however, is not acted on. No trace of ketonic chloride or bromide is obtained by passing hydrogen chloride or bromide into benzene solutions of the hydroxy-alcohol or of its ethers.

On treatment with dilute nitric acid (1 part of conc. acid to 3 parts of water), the hydroxy-alcohol is oxidised to Carstanjen's dibromoparaxyloquinone (Abstr., 1882, 612), and on reduction with sodium amalgam, in alkaline solution, yields a compound $C_9H_{12}O$ which melts at 183—184°.

The author has succeeded in synthesizing the hydroxy-alcohol from Fittig's 2 : 5 : 3-dibromonitroparaxylene (*Annalen*, 1868, **147**, 28; compare Jannasch, *Ber.*, 1877, **10**, 1356). A small quantity of the 3 : 6-*dinitro*-compound was also obtained on the nitration of dibromoparaxylene. It crystallises in colourless needles, and melts at 255°.

2:5:3-*Dibromamidoparaxylene* is obtained by reducing the mononitro-compound with iron and acetic acid. It is best purified by extracting the acid solution with ether, and then converting the base into its hydrochloride by passing hydrogen chloride into the ethereal solution. The hydrochloride is decomposed by boiling with water, and the base set free. It crystallises in small, colourless needles, melts at 91—92°, and is readily soluble in all organic solvents.

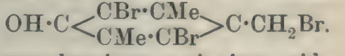
The corresponding 2 : 5-*dibromo*-1 : 4 : 3-*xylenol* is obtained in largest quantity on diazotising the amido-compound by Knoevenagel's method (Abstr., 1891, 54), and then adding the diazo-salt to a mixture of sulphuric acid and water heated at 110—120°, as recommended by Schmidt. Crystallised from light petroleum, it forms small needles, and melts at 90—91°. Its *benzoate* melts at 133·5°. It readily condenses with formaldehyde when treated according to the Lederer-Manasse method. The 3 : 6-dibromo-4-hydroxy-2 : 5-dimethylbenzylic alcohol thus obtained is identical with the hydroxydibromo-ψ-cumenol previously described.

The tribomo-derivative of ψ-cumenol when shaken with an aqueous solution of sodium sulphide yields the *sulphide*

$$(OH\cdot C_6Br_2Me_2\cdot CH_2)_2S.$$

It crystallises in long, colourless needles, melts at 243—245°, and is only sparingly soluble in most organic solvents. On oxidation with dilute nitric acid, it yields dibromoparaxyloquinone. When heated at 100° with methylic alcohol, methylic iodide, and alkali, it yields the *dimethoxy*-compound, $(OMe\cdot C_6Br_2Me_2\cdot CH_2)_2S$, which melts at 169°.

The dibromo-ψ-cumenol bromide, when treated with isobutyric acid and potassium isobutyrate yields an *isobutyrate*, which melts at 103—105°, and in most of its properties resembles the corresponding acetate.

The tribromo-ψ-cumenol bromide which is insoluble in alkalis (Abstr., 1896, i, 423) is shown to be  $OH\cdot C\left<\begin{matrix}CBr\cdot CMe\\ CMe\cdot CBr\end{matrix}\right>C\cdot CH_2Br.$ On oxidation, it yields the same dibromoparaxyloquinone as its isomeride which is soluble in alkalis. It moreover yields a *benzoate* which melts at 122°.

J. J. S.

Amidodiphenylic Sulphides. By RUDOLF NIETZKI and HEINRICH BOTHOF (*Ber.*, 1896, **29**, 2774—2775. Compare Abstr., 1895, i, 132).—The production of dinitrophenylic sulphide by the action of sodium sulphide on paranitrochlorobenzene in alcholic solution is not applicable to the meta-compound; sodium sulphide and metanitrochlorobenzene yield Laubenheimer's dichlor-azoxybenzene.

Orthodinitrophenylic sulphide is obtained from orthonitrochlorobenzene and sodium sulphide; it crystallises in golden, lustrous leaflets, and melts at 122—123°. *Orthodiamidophenylic sulphide* is formed on reducing the nitro-compound, and crystallises from hot water in colourless needles melting at 85—86°; the *diacetyl* derivative melts at 160°, and the *dibenzoyl* derivative at 162—163°. This thioaniline is not identical with Hofmann's paradiamidophenylic sulphide (Abstr., 1895, i, 87), although the two substances melt at the same temperature. M. O. F.

Mercuriobenzylammonium Salts. By LEONE PESCI (*Gazzetta*, 1896, **26**, ii, 54—75).—*Mercuriobenzylammonium hydrate*,

$$HgNH(CH_2Ph)\cdot OH,$$

is obtained in solution by adding the calculated quantity of baryta water to a solution of the corresponding sulphate or by treating the corresponding chloride with silver oxide; it is a strong base and decomposes many salts of alkalis. The aqueous solution has an odour of benzylamine and an alkaline reaction, and absorbs carbonic anhydride from the air, depositing a white, amorphous powder. It reacts with sodium thiosulphate and potassium iodide in accordance with the equations $HgNH(CH_2Ph)\cdot OH + H_2O + Na_2S_2O_3 = HgS_2O_3 + 2NaOH + NH_2\cdot CH_2Ph$ and $HgNH(CH_2Ph)\cdot OH + H_2O + 2KI = HgI_2 + 2KHO + NH_2\cdot CH_2Ph$.

On adding benzylamine to aqueous mercuric chloride, a white *precipitate* is deposited having the composition

$$6HgNH(CH_2Ph)Cl,NH_2\cdot CH_2Ph,HCl;$$

when prepared in alcoholic solution, the precipitate contains only half the above proportion of mercuriobenzylammonium chloride. Mercuric chloride and benzylamine, in molecular proportion, react with formation of mercuriobenzylammonium chloride and benzylamine hydrochloride, and the latter is in part tenaciously held by the former. The double salt, $6HgNH(CH_2Ph)Cl,NH_2\cdot CH_2Ph,HCl$, when treated with very dilute potash, yields benzylamine and *mercuriobenzylammonium chloride*; the latter is a white, amorphous powder insoluble in the ordinary solvents, and is decomposed by potassium iodide, ammonium bromide and sodium thiosulphate solutions in accordance with the equations $HgNH(CH_2PH)Cl + 2KI + H_2O = HgI_2 + KCl + KHO + NH_2\cdot CH_2Ph$ and $HgNH(CH_2Ph)Cl + 2NH_4Br = HgBr_2 + 2NH_3 + NH_2\cdot CH_2Ph$ and $HgNH(CH_2Ph)Cl + Na_2S_2O_3 + H_2O = HgS_2O_3 + NaCl + NaOH + NH_2\cdot CH_2Ph$. The compound prepared by André (Abstr., 1891, 1030) by treating mercuric chloride with benzylamine was identical with this chloride.

A double *compound* of the composition

$$HgNH(CH_2Ph)Cl,NH_2\cdot CH_2Ph,HCl,HgCl_2,$$

is prepared by boiling the precipitate obtained from mercuric chloride and benzylamine with mercuric chloride solution; it crystallises in colourless, pearly laminæ insoluble in the ordinary solvents, and is decomposed by hydrogen sulphide with formation of hydrogen chloride, mercuric sulphide and benzylamine hydrochloride. It is decomposed by potassium iodide, ammonium bromide, and sodium thiosulphate, in the same way as the other salts of the base.

Mercuriobenzylammonium sulphate, $(HgNH{\cdot}CH_2Ph)_2SO_4$, is precipitated on adding the calculated quantity of sodium sulphate to a solution of the double acetate described below; it is a white, amorphous powder, insoluble in the ordinary solvents. A double *salt* of the composition $(HgNH{\cdot}CH_2Ph)_2SO_4,(NH_2{\cdot}CH_2Ph)_2,H_2SO_4$, is deposited on adding benzylamine to sulphuric acid; it is a white powder, and is not separated into its constituents by water.

A double *nitrate* of the composition

$$HgNH(CH_2Ph)NO_3,NH_2{\cdot}CH_2Ph,HNO_3,$$

is prepared by boiling the precipitate obtained by adding benzylamine to a slightly acid solution of mercuric nitrate with its mother liquor; on cooling, the salt separates in colourless, brilliant laminæ. Mercuriobenzylammonium nitrate could not be prepared.

A double *acetate* of the composition

$$HgNH(CH_2Ph){\cdot}C_2H_3O_2,NH_2{\cdot}CH_2Ph,C_2H_4O_2,$$

is deposited in lustrous rectangular plates on adding benzylamine to a saturated aqueous solution of mercuric acetate; it may be crystallised from hot water, in which it is very soluble. Mercuriobenzylammonium acetate could not be prepared. W. J. P.

Enantiomorphic Phenethylamines. By JOHAN M. LOVÉN (*Ber.*, 1896, **29**, 2313—2318).—Phenethylamine, $NH_2{\cdot}CHMePh$, prepared from acetophenoxime by reduction, yields two distinct compounds on conversion into the hydrogen tartrate. From the concentrated solution of the salt, slender needles containing $1\frac{1}{2}H_2O$ first separate; these, on reconversion into the base, yield a slightly dextro-rotatory compound (+0·75°). From the mother liquor of the needles, anhydrous prismatic crystals separate after a time, and these on treatment with potash yield a base which is strongly lævo-rotatory (−8·5° in a 200 mm. tube).

The figures given for the rotatory powers do not pretend to any great accuracy, it being merely intended to show the possibility of resolving inactive phenethylamine into its optical components. J. F. T.

Behaviour of Orthonitroparaphenylenediamine towards Nitrous Acid. By CARL BÜLOW (*Ber.*, 1896, **29**, 2284—2287).—It has been observed by Ladenburg that the action of nitrous acid on orthonitroparaphenylenediamine gives rise to a brown, amorphous powder, but the exact nature of the substance has not been investigated. On adding a 20 per cent. solution of sodium nitrite to a solution of orthonitrophenylenediamine hydrochloride in acetic acid, the author has obtained *metanitroparamidodiazobenzene*, along with a very small quantity of the amorphous, brown substance, which is probably a tetrazo-compound. When the diazo-compound is treated with sodium β-naphthol-3 : 6-disulphonate, lustrous, green needles rapidly separate, appearing dark blue by transmitted light.

On adding sodium nitrite to an acid solution of paramidometanitrodiazobenzene, the amido-group is diazotised, the diazonitro-azo-compound separating as a bluish-red precipitate.

Paramidometanitrodiazobenzene and sodium paramidometanitrobenzeneazo-β-naphtholdisulphonate are converted into the corresponding nitrosamines by caustic alkali, these substances being indifferent towards sodium 2-naphthol-3 : 6-disulphonate. Mineral acids, on the other hand, convert them into the diazo-compounds. M. O. F.

Action of Sodium on Aromatic Nitriles. By C. A. ALFRED LOTTERMOSER (*J. pr. Chem.*, 1896, [2], **54**, 113—143).—Walther has shown (Abstr., 1894, i, 503) that when benzonitrile (2 mols.), aniline (1 mol.) and sodium (2 atoms) are heated together in benzene, phenylbenzenylamidine is obtained. The contents of the flask are poured into alcohol to dissolve remaining sodium, and the whole is then diluted with water, acidified with acetic acid, and heated on the water bath until hydrogen cyanide and benzene have been eliminated. By further dilution, some impurities are separated ; these are filtered off and ammonia is added to the filtrate, which is then stirred until the new base is precipitated. The yield is about 84 per cent. of that calculated from the equation $2PhCN + PhNH_2 + Na_2 = C_6H_6 + NaCN + NHPh{\cdot}CPh{:}NNa$. The position of the sodium in the sodium derivative which is first produced has not been determined with certainty. *Diacetophenylbenzenylamidine*, $NPhAc{\cdot}CPh{:}NAc$, is crystalline and melts at 128—130° ; it is produced by heating the amidine with acetic anhydride, a treatment which generally fails to replace both atoms of hydrogen in an amido-group by acetyl, so that the amidine must have the constitution corresponding with the above formula rather than that represented by $NH_2{\cdot}CPh{:}NPh$.

By heating phenylbenzenylamidine with phenylhydrazine hydrochloride, or phenylbenzenylamidine hydrochloride with phenylhydrazine, the *phenylhydrazide*, $NHPh{\cdot}CPh{:}N{\cdot}NPh$ is formed ; it melts at 174°, and is apparently identical with von Pechmann's anilamidobenzenylphenylimidine (Abstr., 1896, i, 32), to which, however, the formula $NPh{:}CPh{\cdot}NH{\cdot}NHPh$ has been assigned, chiefly because of the power that the compound has of reducing mercuric oxide. The *oxime*, $NHPh{\cdot}CPh{:}NOH$, is formed in white needles when hydroxylamine hydrochloride and the amidine are warmed together and ammonia is added by degrees ; it melts at 135—136°.

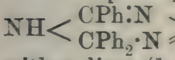
Orthotolylbenzenylamidine, prepared like the phenylamidine, crystallises in small needles, melts at 105—108°, and dissolves freely in alcohol, ether, and chloroform, less freely in benzene, and very sparingly in light petroleum. Paratolylbenzenylamidine, already described by Bernthsen, is only produced from paratoluidine if ether be substituted for benzene in the prescription for the phenylamidine. When benzene is the solvent, a *compound*, $C_{17}H_{14}N_2$, is produced, which crystallises in lustrous, yellow laminæ, melts at 121—123°, and dissolves easily in ether and chloroform, but only sparingly in alcohol ; the *platinochloride* was prepared. To ascertain whether the para-position of the methyl to the amido-group is the conditioning factor in the abnormal behaviour of paratoluidine, metaxylidine was submitted to the reaction. *Metaxylylbenzenylamidine* was, however, obtained; it crystallises in colourless needles, and melts at 106—107°.

Phenylacetophenylamidine, $CH_2Ph\cdot C(NHPh)\colon NH$, was prepared by the action of sodium on aniline and benzylic cyanide in benzene; it is identical with Bernthsen's compound obtained from benzylic cyanide and aniline hydrochloride (Abstr., 1876, ii, 95); it melts at 139°.

Phenylorthotolenylamidine, prepared from aniline and orthotoluonitrile by the action of sodium, ether being used instead of benzene, melts at 121—123°, and shows nearly the same solubility as the foregoing amidines. *Phenylparatolenylamidine*, similarly prepared, melts at 149°; its *diacetyl*-derivative melts at 121—122°.

Phenyl-β-naphthenylamidine, from aniline and β-naphthonitrile, crystallises in small, lustrous laminæ, and melts at 162—163°. *Phenyl-α-naphthenylamidine* melts at 128—130°.

It is noticeable that the amidines made from benzonitrile, tolunitrile, and naphthonitrile decrease in solubility in alcohol, benzene, ether, chloroform, and light petroleum in the order in which they have been named. This is also the case with the yield of amidine obtainable.

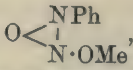
A compound, $C_{27}H_{21}N_3$, believed to be *tetraphenyldihydrotriazine*,  $NH<\begin{matrix}CPh\colon N\\ CPh_2\cdot N\end{matrix}>CPh$, is obtained by heating benzonitrile (2 mols.) with sodium (1 atom) in benzene for several days on the water bath; light petroleum is added, and the precipitate is dried on a clay-plate and added cautiously to water, whereby the sodium cyanide is removed from the insoluble new compound, which is finally crystallised from alcohol. Some cyaphenine is also formed in the reaction. The triazine crystallises in long, white needles, melts at 190—191°, and dissolves sparingly in alcohol, but more freely in benzene, ether, and chloroform. The *hydrogen chromate*, $C_{27}H_{21}N_3,H_2CrO_4$, the *hydrochloride*, $C_{27}H_{21}N_3,HCl$, the *hydrogen sulphate*, and the *platinochloride* (with $1H_2O$) are described. When heated with alcoholic potash, the base yields potassium benzoate, ammonia, and benzophenone; when heated with phenylhydrazine hydrochloride in alcohol, it yields benzophenone hydrazone, ammonium chloride, and benzonitrile. These facts are considered indicative of the constitution ascribed to the compound.

A. G. B.

Phenylhydroxylamine. By Carl Goldschmidt (*Ber.*, 1896, **29**, 2307).—Phenylhydroxylamine is most advantageously prepared by dissolving nitrobenzene in 10 parts of ether containing a few c.c. of water, and heating with excess of zinc dust and some calcium chloride for 3 hours on the water bath. This modification of the method of Wohl and Bamberger gives rise to a product which is free from aniline.

M. O. F.

Nitrosophenylhydroxylamine. By Eugen Bamberger and Thor Ekecrantz (*Ber.*, 1896, **29**, 2412—2414).—The method of obtaining methylic derivatives by means of diazomethane, due to von Pechmann (Abstr., 1895, i, 328, 493), has been applied by the authors to nitrosophenylhydroxylamine.

Nitrosophenylhydroxylamine methyl ether,  $O<\begin{matrix}NPh\\ |\\ N\cdot OMe\end{matrix}$, dissolves readily in cold organic solvents excepting light petroleum, and crystallises in colourless prisms melting at 37—38° ; it is obviously isomeric with the α- and β-methylic salts of benzenediazoïc acid (Abstr., 1894, i, 238), but is distinguished from these compounds by its greater stability, being volatile without decomposition in an atmosphere of steam, and developing no coloration with naphthylamine acetate. M. O. F.

Action of Hydroxylamine on Nitro-compounds. By OTTO W. SCHULTZE (*Ber.*, 1896, **29**, 2287—2290. Compare Abstr., 1896, i, 613).—*Dinitronitrosophenylhydroxylamine*, $C_6H_3(NO_2)_2\cdot N_2O_2H$, is obtained on adding a solution of hydroxylamine hydrochloride, neutralised with sodium carbonate, to symmetrical trinitrobenzene in presence of caustic potash, and cautiously acidifying the cooled solution with hydrochloric acid ; it separates from ethylic acetate in prismatic crystals having a bluish-red reflex, and melts at 184—185°. Hydroxylamine is without action on ortho- or meta-dinitrobenzene.

When nitromethane is dissolved in caustic potash and allowed to remain with excess of hydroxylamine hydrochloride, Lecco's methazonic acid (this Journal, 1876, ii, 287) is formed ; the *potassium* derivative crystallises in beautiful, white needles, and explodes when heated, a bright blue flame being produced.

Ethazonic acid, obtained from nitroethane and hydroxylamine, is a substance which crystallises very readily, and melts at 93°, with rapid disengagement of nitric peroxide. M. O. F.

Constitution of Hydroxyazo-compounds. By KARL AUWERS (*Ber.*, 1896, **29**, 2361—2362. Compare Goldschmidt, Abstr., 1891, 1209, and 1892, 974 ; McPherson, Abstr., 1896, i, 27).—According to Goldschmidt, the hydroxyazo-compounds are all to be regarded as quinone hydrazones, whereas McPherson regards the para-compounds as true hydroxy-derivatives and the ortho-compounds as hydrazones. The author has undertaken an examination of some 20 hydroxyazo-compounds as regards their cryoscopic behaviour in naphthalene solution. The results agree with those drawn by McPherson from chemical considerations.

The para-compounds gave abnormal results, thus indicating their hydroxylic nature (compare Abstr., 1894, ii, 133 ; 1895, ii, 41 ; and 1896, ii, 293). The ortho-compounds gave quite normal results, as did also certain undoubted hydrazones which the author investigated.

These remarks apply only to the free hydroxyazo-compounds and not to their salts or ethers. J. J. S.

Oxidation of Phenylbenzylidenehydrazone. By GAETANO MINUNNI and E. RAP (*Gazzetta*, 1896, **26**, i, 441—456).—On oxidising phenylbenzylidenehydrazone with yellow mercuric oxide in a 4·5 per cent. chloroform solution on the water bath, dehydrophenylbenzylidenehydrazone and a little diphenyldibenzylidenehydrotetrazone are obtained ; the former alone is produced if the oxidation is carried out in an ethereal or a 2 per cent. chloroform solution. Phenylbenzylidenehydrazone is readily oxidised by boiling with amylic nitrite in ethereal solution; in this case, dehydrophenylbenzylidenehydrazone is produced in much greater quantity than the tetrazone.

Diphenyldibenzylidenehydrotetrazone melts at 180—181° in a previously heated bath, but if heated slowly, it is converted into dehydrophenylbenzylidenehydrazone and then melts at 185—190°; the misunderstanding between Minunni (Abstr., 1893, i, 97), von Pechmann (Abstr., 1893, i, 461), and Ingle and Mann (Trans., 1895, 606), arises from this fact. The tetrazone crystallises in thin, yellow needles, and is sparingly soluble in the usual solvents. Dehydrophenylbenzylidenehydrazone crystallises in thin, colourless needles which melt at 198—200° when slowly heated, but at 205° if rapidly heated; it is readily obtained by heating the tetrazone at 180°. In the oxidation with amylic nitrite, these two products are accompanied by small quantities of an oxygenated *compound* crystallising in needles which do not melt at 240°.

On heating diphenyldibenzylidenehydrotetrazone with benzoic chloride on a salt water bath, a *substance*, $C_{14}H_{10}N$, is obtained which crystallises in pearly, white laminæ melting at 211·5—212·5°; on heating the tetrazone with benzoic or acetic chloride on a water bath, the principal product is a crystalline *compound* melting at 178—179°. The substance melting at 211·5—212·5° is also obtained by heating β-benzilosazone with benzoic chloride on a salt water bath.

On heating dehydrophenylbenzylidenehydrazone with benzoic chloride at 100°, a small proportion of the substance melting at 211·5—212·5° is obtained; at lower temperatures a crystalline *compound* melting at 173° and a *monobenzoyl*-derivative, $C_{26}H_{21}N_4\cdot COPh$, of dehydrophenylbenzylidenehydrazone, which crystallises in lustrous, white needles melting at 186—188° are produced. The substance melting at 173° can be converted into the benzoyl derivative by heating it above its melting point. W. J. P.

The Methyl-, Ethyl-, Amyl- Allyl-, and Benzyl-phenylhydrazones, and the β-naphthylhydrazones of the Sugars. By W. Alberda Van Eckenstein and Cornelis A. Lobry de Bruyn. (*Rec. Trav. Chim.*, 1896, **15**, 225—229).—The authors have pointed out (Abstr., 1896, i, 588) that the above hydrazones might be of considerable service in the identification and separation of certain sugars. In the present communication, a list is given in tabular form of the alkylated phenylhydrazones and β-naphthylhydrazones of galactose, mannose, arabinose, rhamnose, glucose, xylose, lactose, maltose, and melibiose, together with their melting points, specific rotatory powers in methylic alcohol and glacial acetic acid solutions, and statements as to their colour and solubility in water and methylic and ethylic alcohols. These compounds were prepared by adding to a hot concentrated solution of the sugar the equivalent quantity of the hydrazine dissolved in the molecular proportion of glacial acetic acid. When boiled with benzaldehyde in aqueous solution, they all undergo quantitative decomposition and may consequently be utilised for the preparation of certain of the sugars in a state of purity. No alkylphenylhydrazones were obtained in the case of fructose, sorbose, maltose and xylose, and of these four, maltose and xylose alone yielded β-naphthylhydrazones. The methyl- and ethyl-phenylhydrazones of glucose and lactose could not be prepared. The benzyl-, allyl- and amyl-hydrazones of galactose have the property of forming jellies when their boiling solutions (0·1—0·25 gram in 25 c.c. water) are rapidly cooled.

A. C. C.

Isomeric Nitrosodiethylphloroglucinols. By D. Moldauer (*Monatsh.*, 1896, 17, 462—478).—A strong solution of diethylphloroglucinol (1 mol.) in caustic potash containing potassium nitrite (2 mols.) is mixed at 0° with acetic acid; the whole, after being allowed to remain during 2—3 hours at the ordinary temperature, is filtered, the insoluble portion washed with ice-cold water to eliminate all inorganic salts, and dried at 50—60°; it is then extracted with absolute ether in which one portion is soluble and the other, which is insoluble, is obtained in the form of slender, light yellow needles.

The ethereal solution, on evaporation, deposits *a-diethoxyquinonoxime*, $C_{10}H_{13}NO_4$, which forms dark red leaflets, melts at 117° (uncorr.), and sublimes at higher temperatures suffering slight decomposition; it dissolves in most media, and with dilute alkalis forms a dark brown solution from which it is precipitated on acidification; it gives Liebermann's nitroso-reaction. The *potassium* salt, $C_{10}H_{12}NO_4K$, crystallises in beautiful, grass-green needles and is soluble in alcohol; the *silver* salt forms minute, reddish-brown crystals insoluble in water.

The insoluble substance *β-diethoxyquinonoxime* crystallises from alcohol or boiling water in small, woolly needles, melts and decomposes at 192—195°, dissolves in alkali forming a reddish-brown solution, and gives Liebermann's reaction. The *potassium* salt, $C_{10}H_{12}NO_4K + H_2O$, forms small, blue-violet crystals, and is excessively soluble in water; the *silver* salt is obtained as a green, microcrystalline precipitate.

The potassium salt of α-diethoxyquinonoxime reacts with ethylic iodide at the temperature of the water bath and the product consists of two salts, which may be separated by fractional precipitation from alcohol. The more soluble portion, *α-diethoxyquinonoxime ethylic ether*, $C_6H_2NO(OEt)_3$, crystallises in small, red, prismatic crystals, melting at 106°; it is slowly dissolved and decomposed by hot water or dilute alkali.

The more sparingly soluble substance crystallises in colourless, shining triclinic tables, melts at 60°, is insoluble in water, but dissolves readily in ether, benzene, and petroleum; it does not give Liebermann's reaction. It has the molecular formula $C_{12}H_{15}NO_3$, and appears to be formed directly from the oxime, as it cannot be obtained from the foregoing substance; it contains, moreover, only two ethoxyl groups. Several provisional constitutions are suggested for it, but for the present the authors prefer to use the name *ethylpyriphlorone diethylic ether*. The following salts have been prepared from it; the *hydrochloride*,

$$C_{12}H_{15}NO_3,HCl,$$

crystallises in long, silky needles, and melts, evolving hydrogen chloride, at 72—78°, and is readily decomposed; the *platinochloride*,

$$(C_{12}H_{15}NO_3)_2,H_2PtCl_6,$$

crystallises from a mixture of alcohol and hydrochloric acid in slender needles.

Ethylic iodide also acts on β-diethoxyquinonoxime; the product consists of a *triethylic* ether, $C_6H_2NO(OEt)_3$, which dissolves readily in nearly all the ordinary media, crystallises in yellow, silky needles, melts at 117—118°, and distils unaltered at higher temperatures, the vapours solidifying to large, colourless needles.

α-Diethoxyquinonoxime is reduced by stannous chloride and hydrochloric acid, an ethyl group being simultaneously removed; the *product* $C_8H_{11}NO_3,HCl$ forms an unstable, white, crystalline mass. The oxime also reacts with phenylhydrazine and with hydroxylamine, yielding, in the former instance, a *substance* which turns brown below 152°.

A. L.

Conversion of α-Aldoximes into Nitriles. By GAETANO MINUNNI and D. VASSALLO (*Gazzetta*, 1896, **26**, i, 456—465).—On treatment with ether saturated with hydrogen chloride at $-10°$, the benzoyl derivatives of α-metanitrobenzaldoxime, α-cuminaldoxime, α-anisaldoxime, α-salicylaldoxime, α-furfuraldoxime and α-propaldoxime are converted into the corresponding nitriles and acids, just as benzoyl- or acetyl-α-benzaldoxime is converted into benzonitrile and benzoic acid (Minunni, Abstr., 1893, i, 89); the reaction is represented by the equation $R\cdot CH\colon NO\cdot CO\cdot R = R\cdot C\vdots N + R\cdot COOH$.

Both α- and β-oximes can therefore be directly converted into the corresponding nitriles at ordinary temperatures, the former by the action of ethereal hydrogen chloride, and the latter by treatment with alkali carbonates; the α-oximes do not previously change into their β-isomerides, for ethereal hydrogen chloride converts β-benzoylbenzaldoxime into the α-modification.

Benzoyl-α-cuminaldoxime, $C_6H_4Pr\cdot CH\colon NO\cdot COPh$, crystallises in long, white needles melting at 125—126°; *cuminonitrile*, $C_6H_4Pr\cdot CN$, is an oil boiling at 239—241°. *Anisonitrile* crystallises in long, white needles melting at 59—60°.

Benzoyl-α-furfuraldoxime, $C_4OH_3\cdot CH\colon NO\cdot COPh$, crystallises in broad, white laminæ melting at 138—138·5°.

W. J. P.

Benzylation of Acetaldoxime. By ALFRED WERNER (*Ber.*, 1896, **29**, 2667).—The bye-product obtained by the author and H. Buss in benzylating acetaldoxime, and supposed by them to be a nitrogen ether (Abstr., 1896, i, 461), is found to be identical with the dibenzylhydroxylamine described by Beckmann and A. Köster (Abstr., 1893, i., 464).

A. L.

The "Beckmann Rearrangement." I. Chlorimido-ethers. By JULIUS STIEGLITZ (*Amer. Chem. J.*, 1896, **18**, 751—761).—The author has made experiments in order to determine to what extent, if at all, the remaining hydrogen atom in the group $-CO\cdot NHBr$ is necessary for the molecular rearrangement of the acid bromamides which occurs when these substances are heated with aqueous alkali. He suggests that the alkali causes a direct loss of hydrogen bromide, producing the group (RCO)N: with a univalent nitrogen atom whose reactivity would be the cause of the separation of the alkyl from the carbon atom in union with the nitrogen, thus producing isocyanates. It is remarked that this assumption makes it possible to satisfactorily explain several important reactions, such as the exchange which occurs when oximes are treated with phosphorus pentachloride (Beckmann rearrangement), and the production of isocyanates from the acid azides on warming them with water or alcohol.

Benzochlorimidoethyl ether (chlorimidoethyl benzoate), OEt·CPh:NCl, was prepared by the action of a mixture of sodium hypochlorite and hypochlorous acid on the hydrochloride of benzimidoethyl ether. It is a colourless, mobile oil, which boils at 130—132° (16 mm.) and is readily soluble in the usual organic solvents, insoluble in water, aqueous acids, and alkalis. Attempts to convert this compound into two stereoisomerides were unsuccessful. In alcoholic solution aqueous ammonia at once causes an evolution of nitrogen ; hydrochloric acid an evolution of chlorine. When benzochlorimidoethyl ether was slowly heated, a vigorous reaction occurred, resulting in the formation of benzonitrile (and decomposition products of ethylic hypochlorite) together with smaller quantities of benzamide and of an aniline derivative which was not identified.

The direct exchange, therefore, of the phenyl group and the chlorine atom (forming ethyl phenylimidochlorformate), if it takes place at all, must occur to a very slight extent. It is possible that such a rearrangement might occur more readily in the case of the stereoisomeride of the compound (? "anti-") used by the author, if it could be prepared.

Benzobromimidoethyl ether was prepared by the action of sodium hypobromite on the benzimidoethyl ether hydrochloride. It is a yellowish oil, gradually decomposed by water, and at once by hydrochloric acid or concentrated aqueous ammonia. When heated, it behaves like the chlorimide, giving benzonitrile as the chief product. These results confirm those obtained by Slosson (Abstr., 1896, i, 216) with the acid chloranilides, and appear to show that the hydrogen atom in the group –CO·NHBr is necessary for the "Beckmann rearrangement." They are also in perfect accord with the interpretation of the reaction given above. A. C. C.

Diacid Anilides. By Henry L. Wheeler (*Amer. Chem. J.*, 1896, **18**, 695—702. Compare Abstr. 1896, i, 478, 609).—The anilides described in this paper were prepared by suspending silver formanilide or mercury acetanilide in dry ether or benzene, and adding the appropriate proportion of acid chloride ; the action was generally complete in a few minutes, and on filtering off the silver chloride or mercuric chloride and evaporating the filtrate the anilide was isolated. These anilides react with alkalis with separation of the lower acid radicle, and formation of the anilide of the higher acid.

Formacetanilide, NPhAc·CHO, forms colourless, prismatic crystals, melts at 56°, and dissolves in alcohol, ether, benzene, and sparingly in light petroleum.

Formopropionanilide, CHO·NPh·COEt, is an oil which does not solidify in a freezing mixture, and decomposes when heated at 18 mm. yielding propionanilide.

Formobutyranilide, $COPr^{a}\cdot NPh\cdot COH$, is also an oil which cannot be solidified or distilled unchanged.

Formostearanilide, $C_{17}H_{35}\cdot CO\cdot NPh\cdot COH$, forms colourless crystals, melts at 61°, and is very soluble in benzene, chloroform, light petroleum, carbon bisulphide, and ether, but less soluble in cold alcohol.

Acetopropionanilide, $NPhAc\cdot COEt$, is a clear, colourless oil which boils at 159—160° (? 18 mm.), and does not solidify; it dissolves readily in ether and benzene.

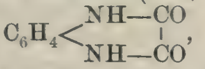
Acetobutyranilide, $COPr^{a}\cdot NPhAc$, is a clear, colourless oil, boiling at 163° (18 mm.).

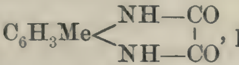
Acetisovaleranilide, $C_4H_9\cdot CO\cdot NPhAc\cdot$, is an oil which boils at 164—165° (18 mm.).

Acetopalmitanilide, $C_{15}H_{31}\cdot CO\cdot NPhAc$, forms colourless, microscopic crystals, and melts at 60—61°.

The action of silver and mercury benzamide on acid chlorides does not yield diacid amides, as might be expected by analogy with the foregoing results; instead, benzonitrile is the chief product.

A. G. B.

Action of Ethylic Oxalate on Aromatic Amido-compounds. By RICHARD E. MEYER and ALB. SEELIGER (*Ber.*, 1896, **29**, 2640—2645).—*Orthophenyleneoxamide*,  $C_6H_4<\begin{matrix}NH—CO\\ |\\ NH—CO\end{matrix}$, is formed when orthophenylenediamine is treated with ethylic oxalate. It forms long, lustrous needles, decomposes at high temperatures without melting, is very sparingly soluble in ether, acetone, benzene and xylene, but dissolves to a considerable extent in petroleum and methylic and ethylic alcohols, separating from these solutions in beautiful crystals. It dissolves readily in dilute aqueous alkalis, and is reprecipitated by carbonic anhydride.

Orthotolyleneoxamide,  $C_6H_3Me<\begin{matrix}NH—CO\\ |\\ NH—CO\end{matrix}$, prepared from orthotolylenediamine $[Me:(NH_2)_2 = 1:3:4]$, crystallises in needles, decomposes without melting when heated, is scarcely soluble in ether, acetone or benzene, but is appreciably dissolved by chloroform, ethylic acetate, light petroleum and xylene, and is soluble in boiling water, methylic and amylic alcohols. Its behaviour towards alkalis resembles that of orthophenyleneoxamide.

Ethylic metaphenylenedioxamate, $C_6H_4(NH\cdot CO\cdot COOEt)_2$, is produced when metaphenylenediamine reacts with ethylic oxalate. It crystallises in small needles, melts at 154°, and dissolves readily in most of the usual media; it is quickly hydrolysed by dilute aqueous alkalis, with production of free *metaphenylenedioxamic acid*, $C_6H_4(NH\cdot CO\cdot COOH)_2$, which crystallises from methylic, ethylic, and amylic alcohols, but is very sparingly soluble in ether, acetone, chloroform, benzene, xylene, and light petroleum; when heated, it sinters, melting finally at 225—230°.

Metaphenylenedioxamide, $C_6H_4(NH\cdot CO\cdot CONH_2)_2$, prepared by treating the foregoing ethylic salt with aqueous ammonia, forms microscopic needles, melting at 290°, is insoluble in the ordinary media, and is hydrolysed by hot soda or strong acids.

Ethylic paraphenylenedioxamate, $C_{14}H_{16}N_2O_6$, resembles the corresponding meta-compound in most particulars, and melts at 215°.

Paraphenylenedioxamide, $C_{10}H_{10}N_4O_4$, froms a crystalline powder and does not melt at 310°.

Orthodihydroxydiphenyloxamide, $C_2O_2(NH{\cdot}C_6H_4{\cdot}OH)_2$, is the product of interaction of orthamidophenol and diethylic oxalate; it crystallises from hot alcohol in yellowish-brown leaflets, melts at 280—282° and is somewhat soluble in methylic, ethylic, and amylic alcohols, but is only sparingly dissolved by benzene and xylene, whilst it appears to be nearly insoluble in light petroleum, ether, and ethylic acetate; it dissolves in alkalis and in hot dilute acids, forming yellow and red solutions respectively. The *diacetyl* compound, $C_2O_2(NH{\cdot}C_6H_4{\cdot}OAc)_2$, melts at 201°.

A. L.

Action of Ammonia and Alkylamines on Bromethylphthalimide. By EUGEN RISTENPART (*Ber.*, 1896, **29**, 2526—2533).—When bromethylphthalimide and diethylamine are heated at 100°, *diethylamidoethylphthalimide* [Phthalyldiethylethylenediamine],

$$C_8H_4O_2{:}N{\cdot}C_2H_4{\cdot}NEt_2,$$

is produced, but has not been isolated on account of its ready solubility; hydrolysis with 20 per cent. hydrochloric acid resolves it into phthalic acid, and *as-diethylethylenediamine*, $NH_2{\cdot}C_2H_4{\cdot}NEt_2$, a mobile, alkaline liquid, which boils at 145°, and has the sp. gr. = 0·827 at 18·5°/18·5°. The *platinochloride* melts at 230°, and the *aurochloride* at 161—163°; the *picrate* melts at 211°, the carbon bisulphide *compound* at 159°, and the *thiocarbamide* at 86°. The action of diethylamine on bromethylphthalimide also gives rise to hydroxyethylphthalimide (Abstr., 1888, 440).

Phthalo-β-bromodiethylamide, $NHEt{\cdot}CO{\cdot}C_6H_4{\cdot}CO{\cdot}NH{\cdot}C_2H_4Br$, is obtained from bromethylphthalimide and ethylamine in alcoholic solution at 0°, and melts at 127°; at higher temperatures *phthalo-ethylvinylamide*, $NHEt{\cdot}CO{\cdot}C_6H_4{\cdot}CO{\cdot}NH{\cdot}C_2H_3$, is produced, and when crystallised from petroleum melts at 106—107°. As in the previous case, hydroxyethylphthalimide is also formed. The *platinochloride* of phthalo-ethylvinylamide melts at 195—196°; the *aurochloride* melts at 125—127°, and the *picrate* at 172°.

Methylamine converts phthalobromethylimide into phthalomethylimide, and ammonia gives rise to β-hydroxyethylphthalimide; along with this substance is formed *triphthalyltriimidotriethylamine*,

$$N(C_2H_4{\cdot}N{<}\genfrac{}{}{0pt}{}{CO}{CO}{>}C_6H_4)_3,$$

which crystallises from glacial acetic acid, and melts at 187·5°. The *hydrobromide* melts at 235°, and the *hydrochloride* at 244·5°. *Triamidotriethylamine*, $N(C_2H_4{\cdot}NH_2)_3$, is obtained by hydrolysing the phthalyl derivative with concentrated hydrochloric acid, and forms a viscous liquid which boils at 263°, under a pressure of 744 mm., and has the sp. gr. = 0·977 at 19°/19°; the *hydrochloride* and *hydrobromide* do not melt below 300°, and the *platinochloride*, which blackens at 250°, melts and effervesces at 280°. The *aurochloride* melts and decomposes at 185°, and the *picrate*, which contains $2H_2O$ at 225°; the *tribenzoyl* derivative crystallises in six-sided plates, and melts at 148—149°. M. O. F.

Derivatives of Amidoguanidine. By GUIDO PELLIZZARI (*Gazzetta*, 1896, **26**, ii, 174—193. Compare Pellizzari and Cuneo, Abstr., 1894, i, 516).—*Benzylideneamidophenylguanidine*, $NH_2 \cdot C(NH) \cdot NPh \cdot N\colon CHPh$, is obtained by treating the aqueous solution of the syrupy amidophenylguanidine (Abstr., 1892, 579) with benzaldehyde; benzylidenephenylhydrazine separates, and on adding an alkali nitrate, *benzylideneamidophenylguanidine nitrate*, $C_{14}H_{14}N_4,HNO_3$, is deposited; it crystallises in long, colourless needles melting and decomposing at 219°. The *picrate* crystallises in yellow needles melting at 242°, whilst the *platinochloride* crystallises in small needles melting at 215°, and is partially reduced on boiling in alcoholic solution. The free base is obtained by treating the nitrate with potash and extracting with ether; it separates in large crystals melting at 133°, and is very soluble in alcohol, benzene, or ether, but only sparingly so in water. It readily changes to an uncrystallisable oil on boiling with benzene, and when treated with potash is converted into benzylidenephenylhydrazine. On boiling an aqueous solution of the nitrate for many hours, benzaldehyde is slowly given off, and pure salts of *amidophenylguanidine*, $NH_2 \cdot C(NH)NPh \cdot NH_2$, can be obtained from the solution. The base is prepared by treating the nitrate with potash; it is an oil which slowly crystallises, and is very soluble in alcohol or ether. It reduces Fehling's solution or ammoniacal silver nitrate, and absorbs carbonic anhydride from the air. The *nitrate*, $C_7H_{10}N_4,HNO_3$, crystallises in hard, colourless, monosymmetric prisms, melting at 143°, and is very soluble in water;

$$a : b : c = 0.5065 : 1 : 0.2567. \ \beta = 85^\circ 47'.$$

The *picrate* crystallises in yellow needles melting at 179°, and is sparingly soluble in water; the *platinochloride* forms small, yellow crystals, and is soluble in alcohol or water. A double *salt* of the composition, $(C_7H_9N_4)_2Cu,2HNO_3$, is obtained by mixing solutions of copper nitrate and amidophenylguanidine nitrate; it crystallises in violet prisms, which lose their water of crystallisation ($3H_2O$?) at 100°.

On boiling paratolylhydrazine hydrochloride with cyanamide in alcoholic solution, paratolylamidoguanidine hydrochloride separates, and amidoparatolylguanidine hydrochloride remains in solution; on shaking the dilute acid solution of the latter salt with benzaldehyde, filtering, and adding potassium or sodium nitrate, *benzylideneamidoparatolylguanidine nitrate*, $NH_2 \cdot C(NH) \cdot N(C_7H_7)N\colon CHPh,HNO_3$, separates as an oil, which ultimately solidifies. It crystallises in hard, transparent, monosymmetric prisms, melting at 214°, and is sparingly soluble in cold water or alcohol;

$$a : b : c = 1.1659 : 1 : 0.8851. \ \beta = 62^\circ 24'.$$

The *picrate*, $C_{15}H_{16}N_4,C_6H_3N_3O_6$, crystallises in yellow needles, melting at 218°, and is sparingly soluble in water or alcohol. The free *base* is obtained as an oil, which soon crystallises, and is soluble in water, alcohol, benzene, or ether.

Amidoparatolylguanidine, $NH_2\cdot C(NH)\cdot N(C_7H_7)\cdot NH_2$, is prepared by boiling the nitrate of its benzylidene derivative with water until benzaldehyde is no longer eliminated. The *nitrate* is obtained in large, white crystals, melting at 110°, and is very soluble in water or alcohol; it combines with benzaldehyde, giving the benzylidene derivative described above, and on treatment with copper nitrate and sodium acetate gives *copper amidoparatolylguanidine nitrate*, which crystallises in sparingly soluble violet needles. The free *base* is obtained as an oil, which soon crystallises; it reduces hot Fehling's solution or ammoniacal silver nitrate.

Phenylamidoguanidine nitrate, $NH_2\cdot C(NH)\cdot NPh\cdot NH_2,HNO_3$, crystallises in needles melting at 178°; it is only sparingly soluble in water or alcohol, and does not combine with benzaldehyde or yield a violet double salt with cupric nitrate. The *picrate* crystallises in yellow needles, melting at 193°, and is sparingly soluble in water or alcohol.

W. J. P.

Are Diphenyliodonium and Thallium Nitrates Isomorphous?

By ARTHUR A. NOYES and C. W. HAPGOOD (*Chem. News*, 1896, **74**, 217).—Saturated solutions of thallous nitrate in water and of diphenyliodonium nitrate in a moderately strong aqueous solution of diphenyliodonium hydroxide were mixed in different proportions, and allowed to crystallise, to a certain extent, in a vacuum; the two salts crystallised out separately, therefore no mixed crystals indicating isomorphism were obtained.

D. A. L.

Chlorophosphines of the Aromatic Series, and their Derivatives.

By C. A. AUGUST MICHAELIS (*Annalen*, 1896, **293**, 193—259. Compare Abstr., 1894, i, 586).—Phenylchlorophosphine has been already described (*Annalen*, 1876, **181**, 265), and has given rise to numerous derivatives; the bromophosphine is also known.

[With HUBERT GLAUBITZ].—*Phenylcyanophosphine*, $PPh(CN)_2$, is obtained by the action of phenylchlorophosphine on silver cyanide at ordinary temperatures, and forms a viscous, colourless liquid, which boils at 144—145° under a pressure of 20 mm.; it is indifferent towards water, but dissolves in dilute alkalis, forming alkali cyanide and alkali phenylphosphinite. *Phenylthiocyanophosphine*, $PPh(CNS)_2$, arises from the action of phenylchlorophosphine on silver thiocyanate; it is a viscous, yellow liquid, which boils at 205—207° under a pressure of 20 mm.

[With KUHLMANN.]—The *diamide* of phenylphosphinic acid,

$$PPhO(NH_2)_2,$$

is produced by the action of concentrated aqueous ammonia on phenyloxychlorophosphine, and crystallises from alcohol in white, lustrous leaflets, melting at 189°.

[With JUNKER.]—The *dianilide* crystallises in white needles, with a bluish tinge, and melts at 211°. *Aniline*-n-*phenylphosphinic acid*, NHPh·PPhO·OH (compare Michaelis, Abstr., 1894, i, 586), is obtained by heating dry aniline hydrochloride with phenyloxychlorophosphine (1 mol.) for 6 hours at 150°, then heating the mixture of chloride and anilide with dilute ammonia, and acidifying with dilute hydrochloric acid; it forms a white, crystalline powder, and melts at 125°. Concentrated hydrochloric acid resolves it into aniline hydrochloride and phenylphosphinic acid. The *phenylic* salt is obtained by the action of phenol on the mixture of chloride and anilide, and forms small, yellowish-white crystals; it melts at 83°, and boils at 235° under a pressure of 25 mm. The *phenylhydrazide* of phenylphosphinic acid, $PPhO(NH·NHPh)_2$, is produced by the action of phenyloxychlorophosphine on phenylhydrazine, and crystallises from alcohol in white needles, which melt at 175°; it is indifferent towards cold Fehling's solution, but reduces it when heated.

[With G. Schlüter.]—*Phenylmethylphosphinic acid*, PMePhO·OH, crystallises from water in white needles, and melts at 133°; it is formed on distilling phenyldipiperidinemethylphosphonium hydroxide (compare Abstr., 1895, i, 682), piperidine being eliminated. The *silver* salt crystallises in lustrous leaflets, and dissolves sparingly in water; it rapidly becomes brown when exposed to light.

[With O. Holle].—*Phenylhydroxyethylphosphinic acid*,

HO·CHMe·PPhO·OH,

is obtained by the action of phenylchlorophosphine on acetaldehyde (1 mol.), and crystallises in stellar aggregates of needles, melting at 104°; the *barium* salt crystallises in silky needles. *Phenylhydroxybenzylphosphinic acid*, HO·CHPh·PPhO·OH, obtained from phenylchlorophosphine and benzaldehyde, melts at 112—114°; the *barium* salt crystallises in small, lustrous plates, and contains $1H_2O$.

[With Wilhelm Maecker.]—*Parachlorophenylchlorophosphine* (*parachlorophosphenylic chloride*), $C_6H_4Cl·PCl_2$, is produced by the action of phosphorus trichloride on chlorobenzene under the influence of aluminium chloride; it is a liquid having the sp. gr. = 1·425 at 17°, and boils at 253—255°. When heated with bromine and water for 2 hours at 150°, it is converted into 1 : 4-chlorobromobenzene and phosphoric acid. Dry chlorine gives rise to *parachlorophosphenylic tetrachloride*, $C_6H_4Cl·PCl_4$, a yellow, hygroscopic, crystalline substance, which resembles phosphorus pentachloride; water converts it into chlorophosphenylic oxychloride, phosphinic acid being ultimately formed. *Parachlorophosphenylic bromochloride*,

$$C_6H_4Cl·PCl_2Br_2,$$

is obtained by the action of dry bromine on parachlorophosphenylic chloride, and melts at 216°; it fumes in the air, and is converted by water into parachlorophenylphosphinic acid. *Parachlorophosphenylic oxychloride*, $C_6H_4Cl·POCl_2$, is formed from the tetrachloride when the liquid is treated with sulphurous anhydride, and subsequently distilled; it is a pale yellow liquid, having the sp. gr. = 1·4892 at 20°, and boils at 284—285°.

Parachlorophenylphosphinous acid, $C_6H_4Cl·PHO·OH$, is produced when parachlorophenylchlorophosphine is added drop by drop to water, hydrogen chloride being eliminated, and crystallises from the solution in long, slender needles or lustrous leaflets, and from alcohol in transparent, quadratic leaflets; it melts at 130—131°, reduces silver solution, and forms a white precipitate with ferric chloride. The *ammonium* salt is deposited from water in lustrous leaflets, and the *barium* salt also forms leaflets containing $1H_2O$; the *copper* salt is blue, and contains $4H_2O$; and the *phenylhydrazine* salt crystallises from dilute, aqueous solutions in long, golden yellow needles, melting at 169°.

Parachlorophenylphosphinic acid, $C_6H_4Cl\cdot PO(OH)_2$, is readily obtained from parachlorophosphenylic tetrachloride and oxychloride by the action of water, the liquid being then evaporated; it crystallises from water in aggregates of silky needles, separating from alcohol in transparent, quadratic plates and melts at 184—185°. The *hydrogen barium* salt forms lustrous, white needles, the *silver* salt is amorphous, and darkens when exposed to light, and the *hydrogen silver* salt crystallises in lustrous leaflets. The *anhydride* (*phosphinoparachlorobenzene*), $C_6H_4Cl\cdot PO_2$, is obtained by heating the finely powdered phosphinic acid with the oxychloride and dry benzene for 2 hours, and forms a white, crystalline powder, which melts at 211°; under the influence of water, it passes into the phosphinic acid.

[With LUDWIG EIFLER.]—*Nitroparachlorophenylphosphinic acid*,

$$NO_2\cdot C_6H_3Cl\cdot PO(OH)_2,$$

is produced by the action of fuming nitric acid on the foregoing phosphinic acid, and crystallises from that agent in long, slender needles; it also forms white, lustrous leaflets, with a pale, yellowish-green reflex. It is soluble in water, and fuses in the hot liquid, but the melting point of the dry substance is 166—168°. The *ammonium* and *potassium* salts are crystalline, the *sodium* salt crystallises in lustrous, yellowish needles, and contains $6H_2O$, and the *barium* salt forms leaflets containing $2H_2O$; the *calcium* and *silver* salts are amorphous and anhydrous. *Amidoparachlorophenylphosphinic acid*,

$$NH_2\cdot C_6H_3Cl\cdot PO(OH)_2,$$

is obtained on reducing the nitro-acid with tin and hydrochloric acid, and crystallises from water in beautiful, lustrous needles; it is insoluble in alcohol and ether, and melts, decomposing, above 270°. The *barium* salt crystallises in colourless leaflets, and contains $1\frac{1}{2}H_2O$; the *silver* salt is a white, amorphous substance, insoluble in water.

Parachlorophenylphosphine, $C_6H_4Cl_4\cdot PH_2$, obtained by distilling parachlorophenylphosphinous acid in an atmosphere of carbonic anhydride, is a white, crystalline mass, which melts at 17° and boils at 198—200°; it becomes oxidised on exposure to air, forming chlorophenylphosphinous acid, and the same compound is produced under the influence of potash. The *platinochloride* is a yellow, crystalline powder, which does not melt below 270°; the *diethyl* derivative boils at 255—257°; and is a colourless liquid with a penetrating odour. The *methiodide* of the latter is a snow-white, deliquescent powder, and melts at 97—98°. *Parachlorophosphenylic chloride phenylhydrazone*,

$$C_6H_4Cl\cdot P\colon N\cdot NHPh,$$

is obtained from the chloride and phenylhydrazine in ethereal solution; it crystallises from benzene in white, lustrous leaflets, and melts and decomposes at 161°.

[With ERICH GUNDERMANN.]—*Parabromophenylchlorophosphine* (*parabromophosphenylic chloride*), $C_6H_4Br{\cdot}PCl_2$, is prepared from bromobenzene and phosphorus trichloride under the influence of aluminium chloride, and forms a somewhat viscous, highly refractive liquid, having a sp. gr. = 1·6895 at 15°; it boils at 271—272°, and when heated with bromine and water yields paradibromobenzene. The *tetrachloride*, obtained by the action of chlorine, is a yellow, crystalline substance, which melts at 55°; the *oxychloride* boils at 290—291°.

Parabromophenylphosphinous acid, $C_6H_4Br{\cdot}PHO{\cdot}OH$, is produced by the action of water on the foregoing chlorophosphine, and crystallises from dilute alcohol in large, white leaflets; it is sparingly soluble in cold water, and melts at 143°. The *potassium* salt forms colourless, quadratic plates, and the *ammonium* salt crystallises in lustrous, white leaflets; the *calcium* salt is deposited from water in crystalline aggregates, and the *barium* salt forms white leaflets containing $1H_2O$. The *lead* and *copper* salts are anhydrous, the *aniline* salt crystallises from water in prisms, and the *phenylhydrazine* salt forms large, lustrous leaflets, which melt and decompose at 181°.

Parabromophenylphosphinic acid, $C_6H_4Br{\cdot}PO(OH)_2$, is obtained by treating the oxychloride with hot water, hydrogen chloride being eliminated; it crystallises in long, lustrous needles, and melts at 202°, yielding metaphosphoric acid and bromobenzene when heated above this temperature. The *hydrogen potassium* salt crystallises in needles, and the *hydrogen barium* salt in white, lustrous leaflets, which contain $1H_2O$; the *silver* salt is amorphous, and the *hydrogen silver* salt resists the action of light, and crystallises in lustrous, white leaflets. The *anhydride* (*phosphinobromobenzene*), $C_6H_4Br{\cdot}PO_2$, is obtained by heating the acid with the oxychloride and benzene until hydrogen chloride is no longer liberated; it is a white powder which melts at 185—186°, and is converted into the acid under the influence of water.

An *isomeride* of parabromophenylphosphinic acid has been isolated from the residue containing aluminium chloride, after separation of the bromophenylchlorophosphine; it crystallises in long, white, lustrous needles, and melts at 265°. The *silver* salt is a white, amorphous powder.

Nitroparabromophenylphosphinic acid, $NO_2{\cdot}C_6H_3Br{\cdot}PO(OH)_2$, is produced by the action of fuming nitric acid on bromophenylphosphinic acid, and crystallises in yellow leaflets; it melts at 185°, and when strongly heated, becomes ignited and chars. The *silver* salt is a white powder.

Parabromophenylphosphine, $C_6H_4Br{\cdot}PH_2$, is formed when parabromophenylphosphinous acid is distilled in an atmosphere of carbonic anhydride; it is a colourless, crystalline mass, which melts at 40° and boils at 195—196°. The *platinochloride* is bright yellow. The *diethyl* derivative boils at 265°, and is a colourless liquid of disagreeable and penetrating odour; the *methiodide* of this substance crystallises in white needles, and melts at 135°, whilst the *ethiodide*, which also forms white needles, melts at 165°. The *phenylhydrazone* of parabromophosphenylic chloride, $C_6H_4Br{\cdot}P{\vdots}N{\cdot}NHPh$, is obtained from the chloride and phenylhydrazine; it separates from benzene in small crystals, and melts at 160°.

[With J. Rabinerson, R. Katzenstein, and Ph. Kunz.]—Paramethoxyphenylchlorophosphine (paranisylchlorophosphine) is obtained by heating methoxybenzene with phosphorus trichloride and commercial aluminium chloride during 4—6 hours (compare Abstr., 1894, i, 586); it is a colourless, highly refractive liquid, having the sp. gr. = 1·0764 at 15°, and boils at 245—253° under a pressure of 12—15 mm. *Anisyltetrachlorophosphine*, $OMe\cdot C_6H_4\cdot PCl_4$, is produced by the action of chlorine, and melts at 35—40°; *anisyloxychlorophosphine*, $OMe\cdot C_6H_4\cdot POCl_2$, is obtained from the tetrachloride by means of sulphurous anhydride, and forms a viscous, yellowish liquid, which boils at 173° under a pressure of 12—15 mm.

Anisylphosphinous acid, $OMe\cdot C_6H_4\cdot PHO\cdot OH$, is produced by the action of water on the chlorophosphine, and crystallises in long, slender, lustrous needles, melting at 112°; the *lead* salt forms lustrous scales, and the *phenylhydrazine* salt crystallises from hot water in beautiful, nacreous leaflets, and melts at 116°.

Anisylphosphinic acid, $OMe\cdot C_6H_4\cdot PO(OH)_2$, is formed when the oxychloride is heated with water until hydrogen chloride ceases to be evolved; it separates from water in large crystals, and melts at 158°. The *hydrogen potassium* salt contains $1H_2O$, the *hydrogen barium* salt is anhydrous, and the *copper* and *silver* salts are also anhydrous; the *ferric* salt is yellow, and contains $3H_2O$, whilst the *nickel* and *hydrogen lead* salts are anhydrous. The *phenylhydrazine* salt crystallises from water. The *anhydride* (*phosphinoanisoïl*), $OMe\cdot C_6H_4\cdot PO_2$, is a white, amorphous powder, and melts at 52°.

Nitranisylphosphinic acid, $NO_2\cdot C_6H_3(OMe)\cdot PO(OH)_2$, is obtained by the action of fuming nitric acid on anisylphosphinic acid, and crystallises from alcohol in slender, colourless needles, melting at 187°; the *hydrogen barium* salt contains $3H_2O$, whilst the *copper* and *basic cobalt* salts are anhydrous.

Anisyldiethylphosphine, $OMe\cdot C_6H_4\cdot PEt_2$, prepared from the chlorophosphine and zinc ethide, is a colourless liquid having the sp. gr. = 0·9978 at 18°, and boils at 266—267°; the *methiodide* melts at 91°, and the *platinochloride* of the corresponding methochloride crystallises in beautiful, brownish prisms, and melts at 142°. The *ethiodide* crystallises in long, colourless needles, and melts at 65°; the *platinochloride* of the corresponding ethochloride forms bright brown crystals, and melts at 148°.

[With R. Katzenstein.]—Para-ethoxyphenylchlorophosphine (paraphenetylchlorophosphine), $OEt\cdot C_6H_4\cdot PCl_2$, prepared from ethoxybenzene, phosphorus trichloride, and aluminium chloride, is a colourless liquid which boils at 266°.

Phenetylphosphinous acid, $OEt\cdot C_6H_4\cdot PHO\cdot OH$, is obtained by the action of water on the chlorophosphine, and crystallises in white, lustrous leaflets, melting at 115°. *Phenetylphosphinic acid*,

$$OEt\cdot C_6H_4\cdot PO(OH)_2,$$

prepared from the tetrachloride, crystallises in white needles, and melts at 165°; the *silver* salt is a white, crystalline substance.

Phenetyldiethylphosphine, $OEt\cdot C_6H_4\cdot PEt_2$, is a colourless liquid which boils at 275°, and has a disagreeable odour; the *methiodide* melts at 60°, and the *platinochloride* of the corresponding methochloride crystallises from water in needles, and melts at 208°. M. O. F.

Derivatives of Metadi-iodoparahydroxybenzaldehyde. By CARL PAAL and L. MOHR (*Ber.*, 1896, 29, 2302—2307. Compare Abstr., 1896, i, 40).—Metadi-iodoparahydroxybenzaldehyde forms well-defined alkali derivatives. The *sodium* derivative crystallises from water in long, white needles, and is sparingly soluble in aqueous alkalis, ethylic alcohol, and methylic alcohol; the *silver* derivative is a yellowish powder which dissolves readily in ammonia, but is insoluble in water.

Metadi-iodoparahydroxybenzoic acid, $OH\cdot C_6H_2I_2\cdot COOH$, first obtained by Peltzer (*Annalen*, 146, 294), is produced on oxidising metadi-iodoparahydroxybenzaldehyde with alkaline potassium permanganate; it crystallises from alcohol in white needles, and melts at 237°.

Metadi-iodoparahydroxybenzaldoxime, $OH\cdot C_6H_2I_2\cdot CH\colon NOH$, crystallises from alcohol in white needles, and melts at 203°; it is a stable compound, and has not been converted into the nitrile. *Metadi-iodoparahydroxybenzylidenephenylhydrazone*, $OH\cdot C_6H_2I_2\cdot CH\colon N\cdot NHPh$, crystallises from alcohol in yellow needles, and melts at 160°. *Metadi-iodoparahydroxybenzylideneaniline*, $OH\cdot C_6H_2I_2\cdot CH\colon NPh$, crystallises from alcohol in beautiful violet plates, having metallic lustre; it contains 1 mol. C_2H_6O, which is lost at 100°, and it melts at 169°. *Metadi-iodoparahydroxybenzylideneparatoluidine* crystallises in blue leaflets having metallic lustre, and melts at 189°. *Metadi-iodoparahydroxybenzylidene-α-naphthylamine* forms orange plates melting at 156°, and *metadi-iodoparahydroxybenzylidene-β-naphthylamine* separates from alcohol in red crystals, and melts at 165°.

Metadi-iodoparahydroxybenzylideneacetone, $OH\cdot C_6H_2I_2\cdot CH\colon CH\cdot COMe$, is obtained by the action of acetone on the aldehyde under the influence of concentrated caustic soda; it crystallises in aggregates of white needles, and melts at 168°.

Metadi-iodoparahydroxycinnamic acid, $OH\cdot C_6H_2I_2\cdot CH\colon CH\cdot COOH$, is formed when metadi-iodoparahydroxybenzaldehyde is heated with acetic anhydride and anhydrous sodium acetate for 10—12 hours at 130—140°; it crystallises from ethylic acetate in lustrous, white needles, and melts at 245°. The *silver* salt is a white powder, insoluble in water; the *methylic* salt crystallises from alcohol in small, white needles, and melts at 107°. M. O. F.

New Derivatives of Parahydroxybenzaldehyde, of Paracyanophenol and of Parahydroxybenzoic Acid. By KARL AUWERS and JULIUS REIS (*Ber.*, 1896, **29**, 2355—2360. Compare Paal, Abstr., 1895, i, 40 and 225).—3 : 5 : 4-*Dichlorohydroxybenzaldehyde*, obtained by passing dry chlorine into an acetic acid solution of the hydroxyaldehyde, crystallises in colourless needles, melts at 156°, and is sparingly soluble in benzene, chloroform and light petroleum but readily in alcohol, ether and ethylic acetate. In order to prepare the substituted para-cyanophenols the corresponding substituted hydroxy-aldehydes were converted into their oximes and the latter on boiling for 2 hours with acetic anhydride were converted into the acetyl derivatives of the hydroxy-nitriles.

3 : 5 : 4-*Di-iodohydroxybenzaldoxime* crystallises in small, colourless needles and melts at 192°. It is readily soluble in most organic solvents, only sparingly, however, in ether and light petroleum.

3 : 5 : 4-*Dichlorhydroxybenzaldoxime* melts at 185° ; it is readily soluble in alcohol, ether, and ethylic acetate, sparingly soluble in benzene and chloroform and insoluble in light petroleum.

3 : 4-*Bromacetoxybenzonitrile* crystallises in colourless needles and melts at 100—101°.

The following compounds have also been prepared.

3 : 5 : 4-*Dichloracetoxybenzonitrile*, melting at 93° ; 3 : 5 : 4–*Dibromacetoxybenzonitrile*, melting at 150°, and the corresponding *di-iodo* compound, melting at 198°.

3 : 4-*Bromohydroxybenzonitrile*, melting at 155° ; 3 : 5 : 4-*dichlorohydroxybenzonitrile*, melting at 146° ; the corresponding *dibromnitrile*, melting at 187°, and *di-iodonitrile*, melting at 205—206°. These compounds were obtained by hydrolysing the acetyl derivatives with 4 per cent. alcoholic solution of sodium.

Methylic 3 : 4-*bromohydroxybenzoate* distils at 163—166° under 16 mm. pressure and melts at 107°.

Methylic 3 : 5 : 4-*dibromohydroxybenzoate* melts at 125° and *methylic* 3 : 5 : 4 *di-iodohydroxybenzoate* melts at 167°. J. J. S.

Derivatives of Piperonal. By Carl Goldschmidt (*Ber.*, 1896, **29**, 2328).—*Piperonalphenylmethylhydrazone* is formed when molecular quantities of piperonal and *as*-phenylmethylhydrazine are heated together in an oil bath at 150° ; it consists of white needles, melting at 85°, and is insoluble in water and non-poisonous.

Piperonalparaphenetidine, produced in an analogous manner, forms white, glistening plates melting at 105°. It is insoluble in water, and is only very slightly poisonous. J. F. T.

Regularities in the Behaviour of the Di-ortho-substituted Aromatic Carbonyl Compounds. By Victor Meyer and G. Pavia (*Ber.*, 1896, **29**, 2564—2569).—From experimental data the following law is formulated. "That double acetylation takes place almost quantitatively when both acetyl groups must enter between two ortho-methyl groups, but acetylation does not occur when this cannot be the case ; when one acetyl group can enter between two such methyl groups, although from the constitution of the hydrocarbon it is not necessary that it should do so, further acetylation will occur only to a limited extent."

From this it follows that, in a compound containing an acetyl group in the ortho-position relatively to two methyl groups, a further acetyl group can be made to enter.

Benzene, acetophenone, and ortho- or para-xylene do not under any circumstances yield diacetyl derivatives ; metaxylene gives about 2·3 per cent. of the diacetyl compound, although on repeating the operation several times a large quantity of this compound can be obtained.

From this it would appear that in the acetylation of metaxylene, a small quantity of the compound [$Me_2 : Ac = 1 : 3 : 2$] is produced.

2 : 4-*Diacetylmetaxylene*, $C_6H_2Me_2Ac_2$, forms slender, white needles melting at 108° and boiling at 306°. Mesitylene, durene and isodurene are instances in which an acetyl group can only enter in the ortho-position to two methyl groups, these compounds, therefore, yield on further acetylation 100 per cent. of the diacetyl derivative.

Since the acetyl compound of pseudocumene cannot be further acetylated, it would follow that in the acetylation of pseudocumene, the acetyl group does not enter in position 2.

Symmetrical triethylbenzene and ethylmesitylene readily yield diacetyl derivatives.

It is therefore possible by this means to ascertain quickly and with small quantities of substance whether tri- or tetra-alkylated benzene derivatives are substituted in the positions 1 : 3 : 5 or not.

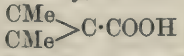
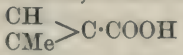
The authors incline to the opinion that mesitylene obtained from acetone is a homogeneous substance and is not admixed with hemellithene.

Mesitylene is completely converted into its diacetyl derivative, whilst hemellithene only yields a monacetyl compound. No fraction of the "mesitylene from acetone" could be obtained which did not yield a diacetyl derivative. Mesitylene is only first partly transformed into an isomeride on carboxylation; a similar instance has been previously noticed in the carboxylation of durene. J. F. T.

Formation of Ethereal Salts. By Rudolf Wegscheider (*Ber.*, 1896, **29**, 2301).—In connection with a recent discussion of Victor Meyer's law, by Angeli, the author points out that identical views were formulated by him in an investigation of hemipinic acid and its ethereal salts (Abstr., 1895, i, 420; compare also i, 499). The publications in question had not met the notice of Angeli.

M. O. F.

Durenecarboxylic Acids. By Victor Meyer and Lothar Wöhler *Ber.*, 1896, **29**, 2569—2573).—It is found that by avoiding an excess of aluminium chloride and by working quickly, no intramolecular rearrangement ensues when durene is converted into its carboxylic acids by Gattermann's method.

It is further shown that the three durenecarboxylic acids behave in accordance with the law of etherification, namely, that the acids of durene and iso-durene which contain the group  $\genfrac{}{}{0pt}{}{CMe}{CMe}\!>\!C{\cdot}COOH$ give no ethylic salt when treated by E. Fisher's method, whilst the carboxylic acid of prehnitol containing the group  $\genfrac{}{}{0pt}{}{CH}{CMe}\!>\!C{\cdot}COOH$ is converted quantitatively into the ethylic salt under these conditions.

Durenecarboxylic acid, which has never before been obtained possessing an absolutely sharp melting point, has now been purified by converting it into the methylic salt (m. p. 58°) and rehydrolysis. The acid prepared in this way melts quite sharply at 176·5°, and on distillation with lime yields pure durene (m. p. 78°). J. F. T.

Action of Ammonia on Alkylic Phenyldibromopropionates. By H. Baucke (*Rec. Trav. Chim.*, 1896, **15**, 128—134).—Ethylic phenyldibromopropionate, $CHPhBr\cdot CHBr\cdot COOEt$, when heated to 45° in sealed vessels for about 2 hours with an excess of aqueous ammonia, previously saturated at 0° with ammonia, yields a small quantity of Anschütz and Selden's bromocinnamamide, $CHPh{:}CBr\cdot CO\cdot NH_2$ (Abstr., 1887, 829), melting at 118°, together with larger quantities of *ethylic monobromocinnamate.* The mixture is best separated by dissolving it in benzene and adding light petroleum when the amide separates in the form of small crystals, whilst the mother liquor on evaporation yields the ethylic salt which distils at 179—180° (28 mm. pressure); this, when hydrolysed with alcoholic potash, yields a mixture of α-bromocinnamic acid (m. p. 120°) and allo-α-bromocinnamic acid (m. p. 131°).

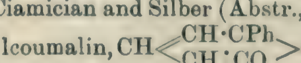
When ethylic phenyldibromopropionate and aqueous ammonia are heated together under the same conditions, but for a longer time, namely, about 3 days, the only product is *α-amidocinnamamide*, $CHPh{:}C(NH_2)\cdot CO\cdot NH_2$, which crystallises from ethylic alcohol, in which it is readily soluble, in rhombic plates and melts at 172°. When hydrolysed, it yields an *acid* melting at 160°; this has not been further investigated.

The author shows, in conclusion, that the bromocinnamamide melting at 118°, is, most probably, a derivative of α-bromocinnamic acid (m. p. 120°) and not of the α-allo acid, and also that the α-amidocinnamide is to be regarded as a derivative of the same acid. J. J. S.

Phenylpropiolamide. By H. Baucke (*Rec. Trav. Chim.*, 1896, **15**, 123—127).—*Phenylpropiolamide* is best obtained by mixing methylic or ethylic phenylpropiolate (Liebermann and Sachse, Abstr., 1891, 1483) with an excess of aqueous ammonia, saturating the mixture with gaseous ammonia at −3°, and keeping it in sealed tubes at 8° for 30 hours. When recrystallised from boiling water, it melts at 102° (compare Stockhausen and Gattermann, Abstr., 1893, i, 164). If treated with a solution of potassium hypobromite, it yields the *potassium* derivative of the *bromamide*, $CPh{\vdots}C\cdot CO\cdot NKBr$, the solution of which when treated with cooled 1 per cent. acetic acid gives a white precipitate of *phenylpropiolbromamide.* The *silver* salt also forms a white precipitate.

All attempts to convert this bromamide into the amine, $CPh{\vdots}C\cdot NH_2$, by means of alkalis proved futile. J. J. S.

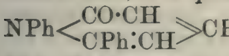
Phenylcoumalin. By Ferruccio Severini (*Gazzetta*, 1896, **26**, ii, 326—350).—The author has examined the supposed α-phenylcoumalin isolated from coto bark by Ciamician and Silber (Abstr., 1894, i, 300), and shows it to be really α-phenylcoumalin,

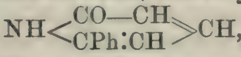


$CH\Big<{}^{CH\cdot CPh}_{CH:CO}\Big>O$; it is obtained as a yellowish microcrystalline powder, which has an aromatic odour, and melts at 68°. When heated in sealed tubes, at 110° with concentrated hydrochloric acid, it is converted into a *polymeride* $(C_{11}H_8O_2)_2$, which forms a white, crystalline powder melting and decomposing at 219°; its molecular weight was determined by the cryoscopic method in benzoic acid solution. Phenylcoumalin yields phenylvaleric acid on reduction with sodium amalgam.

Phenylcoumalin picrate, $C_{11}H_8O_2,C_6H_2(NO_2)_3\cdot OH$, crystallises in beautiful, yellow, anorthic crystals melting at 81—82°; $a:b:c = 1\cdot3443:1:1\cdot7030$. $\alpha = 107°17'$, $\beta = 114°14'$, $\gamma = 63°30'$. Cryoscopic determinations show it to be dissociated in acetic acid solution, just as are the picrates of cotoïn and the dihydroxybenzenes. The *salicylate*, $C_{11}H_8O_2,C_6H_4(OH)\cdot COOH$, is obtained in colourless crystals melting at 93°.

Phenyldimethylcoumalin combines with quinol, giving a white, flocculent crystalline *substance*, $C_{13}H_{12}O_2,C_6H_4(OH)_2$, melting at 113°, and when heated in a closed tube with concentrated hydrochloric acid is partly converted into a resinous mass.

Phenylcoumalin combines with boiling aniline giving a *compound* of the composition $C_{11}H_8O_2,2NH_2Ph$; this crystallises from benzene in white needles which melt at 115—118°, and contain benzene of crystallisation, whilst from alcohol it is obtained in pyramids melting at 142°. On boiling the aniline compound with concentrated hydrochloric acid, it is quantitatively converted into 1 : 2-*diphenyl*-6-*pyridone*,  $\mathrm{NPh}{<}\begin{smallmatrix}\mathrm{CO\cdot CH}\\ \mathrm{CPh{:}CH}\end{smallmatrix}{\geqslant}\mathrm{CH}$, which crystallises in white needles, melting at 144—146°; it is insoluble in water, but very soluble in benzene.

2-*Phenyl*-6-*pyridone*,  $\mathrm{NH}{<}\begin{smallmatrix}\mathrm{CO{-}CH}\\ \mathrm{CPh{:}CH}\end{smallmatrix}{\geqslant}\mathrm{CH}$, may be prepared by boiling phenylcoumalin with ammonium acetate and glacial acetic acid; it crystallises in yellow scales melting at 197° and is soluble in hot water or alcohol, but insoluble in ether. Its *hydrochloride* crystallises in yellow needles melting at 104°, and, together with the platinochloride and aurochloride, is decomposed by water. On distilling 2-phenyl-6-pyridone with zinc dust, it yields 2-phenyl-6-pyridine; the picrate of the latter melts at 175°, and the *platinochloride* crystallises with $2H_2O$ in yellow needles melting at 204°. The pyridone is converted into 6-*chloro*-2-*phenylpyridine* on heating in a closed tube with phosphorus trichloride for 6 hours at 150°; it crystallises in white needles melting at 34°, and has an odour resembling that of pyridine. The platinochloride and aurochloride are crystalline. W. J. P.

Phenylcoumalin. By OSWALD HESSE (*Ber.*, 1896, **29**, 2322—2323).—A reply to Leben (Abstr., 1896, i, 574.) The author affirms the accuracy of the melting point, 61—62°, he gave for phenylcoumalin; the higher melting point (68°) of Ciamician and Silber must be due to some error. J. F. T.

[Phenylcoumalin.] By GIACOMO L. CIAMICIAN and PAUL G. SILBER. (*Ber.*, 1896, **29**, 2659—2662).—A reply to Hesse (preceding abstract). The authors maintain the correctness of the melting point they originally assigned to phenylcoumalin, and draw attention to the uncertainty of the methods used by Hesse to establish the purity of his substance. A. L.

Decomposition of the Phenolic Acids derived from Benzene and Naphthalene. By PAUL CAZENEUVE (*Bull. Soc. Chim.*, 1896,

[3], **15**, 72—82).—The fatty acids and the carboxylic acids derived from cycloid hydrocarbons, when heated with aniline, give rise to anilides. When, however, phenolic hydroxyl groups are present, the compounds tend to decompose into carbonic anhydride and the phenol from which they are derived. Further, the phenolic acids decompose more easily in the presence of aniline than under the same conditions in the presence of water. From the results of his experiments, the author deduces the following laws.

(1) The stability of the carboxyl group in the phenolic acids decreases with the number of hydroxyl groups present in the molecule; the stability is further decreased by the introduction of halogen atoms.

(2) Phenolic acids most easily decompose when the hydroxyl is in the ortho-position, the metahydroxy-acids are the most stable. In the case of dicarboxylic acids, the carboxyl group in the meta-position is the least easily broken off.

(3) Ethereal salts are more stable than the acids themselves; displacement of the hydrogen of hydroxyl by a radicle has the same effect. M. W. T.

Bromoprotocatechuic Acid and the three Isomeric Bromoveratric and Nitroveratric Acids.

By E. C. Theodor Zincke and Bruno Francke (*Annalen*, 1896, **293**, 175—193).—Protocatechuic acid is most conveniently brominated in glacial acetic acid solution, the initial product being 5-bromoprotocatechuic acid, whilst excess of the halogen converts it into tribromocatechuic acid and tetrabromocatechol; hydriodic acid and phosphorus reduce the bromo-derivative to the original acid, and concentrated nitric acid oxidises it to dibromo-β-naphthaquinone-2-carboxylic acid. *Diacetylbromoprotocatechuic acid* is obtained by heating it with acetic chloride in sealed tubes; it crystallises from water in small, white needles, and melts at 187°. The *methylic* salt of bromoprotocatechuic acid crystallises from methylic alcohol, and melts at 201—202°.

5-*Bromoveratric acid*, $COOH\cdot C_6H_2Br(OMe)_2$, is obtained in the form of its methylic salt when methylic bromoprotocatechuate is heated with methylic iodide and sodium methoxide; it is also formed when nitroveratric acid is reduced with tin and concentrated hydrobromic acid. It crystallises from methylic alcohol or glacial acetic acid, and melts at 191°; the *methylic* salt crystallises in beautiful, four-sided prisms, and melts at 71—72°.

6-*Bromoveratric acid* was produced by Koelle (*Annalen*, 1871, **159**, 244) and Matsmoto (Abstr., 1878, 502) by the direct bromination of veratric acid, and has been now obtained in the form of its methylic salt by the action of bromine on ethylic veratrate in glacial acetic acid solution, and also by diazotising ethylic 6-amidoveratrate, and treating the product with cuprous bromide; it melts at 183—184°, and the *methylic* salt crystallises from methylic alcohol and melts at 88—89°.

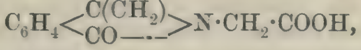
2-*Bromoveratric acid*, obtained by the action of cuprous bromide on diazotised 2-amidoveratric acid (Kuhn, Abstr., 1895, i, 367), crystallises from alcohol, acetone, or glacial acetic acid in needles, and melts at 201—202°; the *methylic* salt is crystalline, and melts at 46°.

The *methylic* salt of 6-amidoveratric acid is formed on reducing the corresponding nitro-compound with tin and hydrochloric acid; it crystallises from benzene in lustrous, monoclinic plates, and melts at 133°.

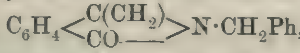
5-*Nitroveratric acid* is obtained from eugenol by nitration, methylation of the potassium nitro-eugenol first prepared by Weselsky and Benedikt, and subsequent oxidation of this substance; it separates from hot solvents in slender, white needles, and melts at 194°. When this acid is reduced, the resulting amidoveratric acid diazotised, and the liquid heated, hydroxyveratric acid is formed, and may be readily converted into the trimethyl ether of methylic gallate. The *methylic* salt of 5-nitroveratric acid forms slender needles, and melts at 78°; reduction with tin and hydrochloric acid converts it into amidoveratric acid. M. O. F.

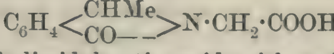
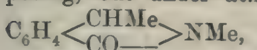
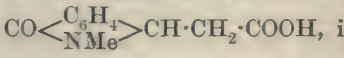
Action of Glycocine on Acetophenone-orthocarboxylic Acid.

By SIEGMUND GABRIEL and GEORG GIEBE (*Ber.*, 1896, **29**, 2518—2525).—*Methylenephthalimidylacetic acid,*



$$C_6H_4<\begin{matrix}C(CH_2)\\CO\end{matrix}>N\cdot CH_2\cdot COOH,$$

obtained by heating glycocine with acetophenonecarboxylic acid in molecular proportion at 160°, crystallises in thick prisms, which melt with effervescence at 199—200°; the *methylic* salt sinters at 102—103°, and melts at 105—106°; the *silver* salt crystallises in beautiful, white needles, and other metallic salts are well defined. When the acid is distilled, methylenephthalomethimidine (Gabriel, Abstr., 1885, 1228) is produced; it is also formed when acetophenonecarboxylic acid is heated with methylamine. The *ethylic* salt of acetophenonecarboxylic acid, which boils at 279°, yields *methylenephthalobenzylimidine,*  $C_6H_4<\begin{matrix}C(CH_2)\\CO\end{matrix}>N\cdot CH_2Ph$, when heated with benzylamine; this crystallises from ethylic acetate in lustrous prisms, and melts at 122°.

Methylphthalimidineacetic acid,  $C_6H_4<\begin{matrix}CHMe\\CO\end{matrix}>N\cdot CH_2\cdot COOH$, is formed on reducing methylenephthalimidylacetic acid with sodium amalgam, and when crystallised from water contains $1H_2O$, which is removed on heating at 100°; the anhydrous substance melts at 162—162·5°, and the crystals at 124°. The *silver* salt crystallises in lustrous, white needles. The acid distils in a vacuum without decomposing, but under atmospheric pressure 1′ : 2′-*dimethylphthalimidine,*  $C_6H_4<\begin{matrix}CHMe\\CO\end{matrix}>NMe$, is produced; its *aurochloride* crystallises in rhombic leaflets and plates, and melts at 163°. This base is also formed when phthalomethimidineacetic acid,  $CO<\begin{matrix}C_6H_4\\NMe\end{matrix}>CH\cdot CH_2\cdot COOH$, is distilled.

Benzylphthalimidine, which has been hitherto obtained by reducing benzylidenephthalimidine with phosphorus and hydriodic acid, is also formed when the amide of deoxybenzoïncarboxylic acid is reduced with sodium amalgam. M. O. F.

A Forgotten Colour Reaction of Gallic Acid and Tannin. By Erich Harnack (*Arch. Pharm.*, 1896, **234**, 537—542). When a solution of tannin or gallic acid is made alkaline with potash, and a few drops of lead acetate solution are added, a red precipitate, which is slightly soluble in the reagents, is formed. This reaction was first described by Buchner (*Annalen*, 1845, **53**, 357), and ascribed by him to the formation of tannoxylic acid, the composition of which was found by Gerhardt to be $C_7H_6O_6$. The colouring matter which is formed has not been obtained pure, since it very readily decomposes with evolution of carbonic anydride and formation of a brown substance. The author considers that it is probably either a quinone of gallic acid or the corresponding quinhydrone. A. H.

Suggested Existence of two Orthophthalic Acids. By Carl Graebe (*Ber.*, 1896, **29**, 2802—2807. Compare Howe, Abstr., 1896, i, 480).—Following the directions of Howe (*loc. cit.*), the author has failed to obtain more than one modification of orthophthalic acid, and therefore questions the existence of a second form; he points out that the melting point of phthalic acid is indefinite, depending on the rate at which the temperature rises and the quantity of substance employed. Experiments have been made with three specimens of phthalic acid, one of which was obtained from the anhydride by the action of cold caustic soda, another consisting of phthalic acid which had been submitted to prolonged treatment with boiling 30 per cent. caustic soda, whilst the aqueous solution of the third was boiling for several hours; the quantity of each specimen dissolved by 100 parts of absolute alcohol at 18° was approximately the same, amounting in each case to about 11·8 parts.

Hydrogen aniline phthalate is produced on mixing alcoholic solutions of aniline and phthalic acid, the employment of 1, 2, 3 or 4 molecular proportions of the base being without influence on the composition of the product; this is inconsistent with Howe's statement that the aniline salt contains two molecular proportions of the base. It melts at 155°, and at once solidifies, water being eliminated with production of phthalanil; when heated for 20—24 hours at 90°, aniline is removed, and the residue consists solely of phthalic acid, the same result being attained in 4—6 hours at 120—125°.

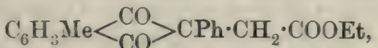
Hydrogen α-naphthylamine phthalate is obtained from phthalic acid and 1, 2 or 3 molecular proportions of α-naphthylamine, and, contrary to the statement of Howe, the normal salt is not produced; it melts at 159—160°, and undergoes no change at 90—100°. When heated at 115—125° for 36—40 hours, the residue consists solely of phthalic acid, whilst exposure to a temperature of 190° converts it in a few minutes into naphthylphthalimide.

Hydrogen quinoline phthalate affords a fresh instance of disagreement with Howe's observations. This substance, which is not associated with a normal salt, melts at 98—99°; it almost completely volatilises at

90—100°, and loses a certain proportion of quinoline when preserved in the exsiccator.

The author is unable to confirm Howe's observations regarding the production of a dihydrophthalic acid differing from Baeyer's $\triangle^{3:5}$-dihydrophthalic acid. He attributes the results which Howe obtained to the presence of a foreign substance in the phthalic anhydride employed, and points out that when phthalic acid is heated during several hours with 30 per cent. caustic soda, a product is formed which contains benzoic acid, unless deposition of solid matter on the sides of the flask is carefully prevented. M. O. F.

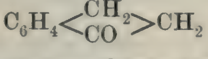
α-Methylphthalic Acid. By OSCAR BLANK (*Ber.*, 1896, **29**, 2376—2381).—*Benzylidenemethylphthalide*, $C_6H_3Me{<}\begin{matrix}C(CHPh)\\ CO\end{matrix}{>}O$, is formed when α-methylphthalic anhydride is heated with phenylacetic acid and sodium acetate. Two isomerides appear to be produced, only one of which has been isolated; this crystallises in slender, light, yellow needles melting at 138°. When this substance is treated in methyl alcoholic solution with sodium methoxide, it passes into 2′:3-*phenylmethyldiketohydrindene*, $C_6H_3Me{<}\begin{matrix}CO\\ CO\end{matrix}{>}CHPh$, which crystallises in colourless needles, softens at 118°, and melts at 131°. The *sodium* derivative readily reacts with alcoholic halogen derivatives and acid chlorides. 2′:3:2′-*Phenyldimethyldiketohydrindene* crystallises in colourless, rhombic plates melting at 123·5°. 2′:3:2′-*Phenylmethylethyldiketohydrindene* melts at 91—93°. 2′:2′:3-*Phenylbenzylmethyldiketohydrindene* forms colourless rhombic plates, and melts at 120—121°. *Ethylic* 2′:3-*phenylmethyldiketohydrindeneacetate*,



$$C_6H_3Me{<}\begin{matrix}CO\\ CO\end{matrix}{>}CPh\cdot CH_2\cdot COOEt,$$

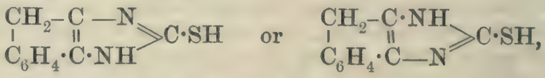
forms colourless crystals, melting at 95—96°. When phenylmethyldiketohydrindene is boiled with alcohol for some time, or oxidised by means of nitrous acid, it is converted into *bis-methylphenyldiketohydrindene*, $C_2Ph_2(\colon C_2O_2\colon C_6H_3Me)_2$, which crystallises in white plates, melting at 209—211°. It is also formed when 2′:2′:3-*bromophenylmethyldiketohydrindene* is boiled with alcohol. This bromo-compound is readily obtained by the bromination of the hydrindene in chloroform solution; it crystallises in slender, white needles, and melts at 76—77°. 2′:2′:3-*Anilidophenylmethyldiketohydrindene* is obtained by the action of aniline on the bromo-derivative. It forms golden yellow needles melting at 169°. 2′:3-*Phenylmethyldiketohydrindenedioxime* crystallises in white plates, and melts and decomposes at 204°. A. H.

β-Amido-α-hydrindone. By SIEGMUND GABRIEL and ROBERT STELZNER (*Ber.*, 1896, **29**, 2603—2608).—α-Hydrindone,



$$C_6H_4{<}\begin{matrix}CH_2\\ CO\end{matrix}{>}CH_2$$

(Abstr., 1889, 1172), was converted into the oxime by treating it in alcoholic solution with amylic nitrite and hydrochloric acid. This derivative yields a brownish-yellow *di-phenylhydrazone,* which melts and decomposes at 228—229°, and is different from the isomeric compound prepared by W. Wislicenus and Kötzle from diketohydrindene (Abstr., 1889, 1067); this shows that the oxime really has the formula, $C_6H_4<\substack{CH_2\\CO}>C:NOH$, assigned to it by Kipping (Trans., 1894, 492), and not the other possible formula, $C_6H_4<\substack{C(NOH)\\—CO—}>CH_2$. It can be reduced with stannous chloride to *β-amido-α-hydrindone,* the *hydrochloride* of which darkens at about 200° and decomposes at 230—240°, whilst the *picrate* decomposes at 152°, and the *platinochloride* darkens at about 200°; the base itself is obtained, more or less impure, as a dark violet powder. When an aqueous solution of the hydrochloride is evaporated with potassium thiocyanate, *orthobenzyleneiminazolylmercaptan,*



$$\begin{matrix}CH_2-C-N\\ C_6H_4\cdot C\cdot NH\end{matrix}\!\!>C\cdot SH \quad\text{or}\quad \begin{matrix}CH_2-C\cdot NH\\ C_6H_4\cdot C—N\end{matrix}\!\!>C\cdot SH,$$

is formed; this decomposes at about 280°.

Amidohydrindone hydrochloride does not react in a similar way with potassium cyanate; it simply yields *α-hydrindonyl-β-carbamide,* $C_6H_4<\substack{CH_2\\CO}>NH\cdot CO\cdot NH_2$, which melts and decomposes at 210—211°.

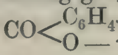
C. F. B.

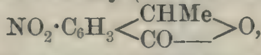
α-Methylphthalide and Orthoethylbenzoic Acid. By GEORG GIEBE (*Ber.*, 1896, **29**, 2533—2543).—Orthoethylbenzoic acid (compare Gabriel and Michael, Abstr., 1878, 427) is obtained by heating methylphthalide with yellow phosphorus and hydriodic acid for 60—65 hours at 137°; it crystallises in long needles, melts at 68°, and boils at 259° under a pressure of 760 mm. The *copper* salt is anhydrous, and the calcium salt contains $3H_2O$; the *ethylic* salt boils at 231° under a pressure of 763 mm., and the *chloride* at 219° under a pressure of 744·5 mm. The *amide* crystallises from water in long white needles, and melts at 151—153°, the *ureïde* melts at 197—198°, and the *nitrile* boils at 212°; *orthoethylthiobenzamide* crystallises from light petroleum in long colourless needles, and melts at 78—79°.

5 : 2-*Nitroethylbenzoic acid,* obtained from ethylbenzoic acid and a mixture of concentrated nitric and sulphuric acids, melts at 164°; 4 : 2-*nitroethylbenzoic acid,* which is produced at the same time, melts at 126°. Each acid yields an ethylic salt which boils about 290°, and in part undergoes decomposition.

5 : 2-*Amidoethylbenzoic acid* is formed on reducing the corresponding nitro-acid with tin and hydrochloric acid, and crystallises from water in colourless needles; it becomes brown on exposure to air, and melts at 179—180°. The substance is also obtained on reducing methylnitrophthalide with red phosphorus and hydriodic acid. 4 : 2-*Amidoethylbenzoic acid* also melts at 179—180°, but differs from the foregoing acid in forming a *sulphate* which is sparingly soluble.

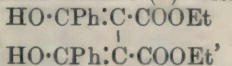
Bis-4 : 2-*nitroethylbenzoylhydrazine,* $N_2H_2(CO\cdot C_6H_3Et\cdot NO_2)_2$, is obtained by the action of 4 : 2-nitroethylbenzoic chloride on hydrazine hydrate; it crystallises from amylic alcohol, is sparingly soluble in ethylic alcohol, and melts, evolving gas, at 245—245·5°.

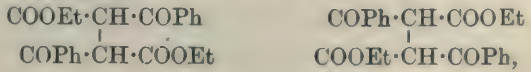
Tetrachloromethylphthalide,  $CO\Big<{}^{C_6H_4}_{O\,—}\Big>CCl\cdot CCl_3$, is obtained by submitting methylphthalide at 200° to the action of a stream of chlorine; it crystallises from 50 per cent. acetic acid, and melts at 90—91°. It is probably identical with the substance obtained from phthalylchloracetic acid by Zincke and Cooksey (Abstr., 1890, 785).

Metanitromethylphthalide,  $NO_2\cdot C_6H_3\Big<{}^{CHMe}_{CO\,—}\Big>O$, produced by the action of fuming nitric acid on methylphthalide in presence of concentrated sulphuric acid, crystallises in small, yellowish needles, and melts at 104°. *Metamidomethylphthalide* is obtained by reducing the foregoing substance with phosphorus and hydriodic acid, and crystallises in long, white needles, melting at 126—127°. M. O. F.

Syntheses with Ethylic Phenylmalonate, II. By WILHELM WISLICENUS and KARL GOLDSTEIN (*Ber.*, 1896, **29**, 2599—2603. Compare Abstr., 1895, i, 368).—Ethylic phenylmalonate, when heated at 100° with alcoholic ammonia, yields a *monamide*, melting at 152°, together with, possibly, a little diamide. When heated with aniline or phenylhydrazine, it yields a *dianilide*, or a *diphenylhydrazide*, melting respectively at 201—202° and 254°, as the case may be. It will not react with methylenic or ethylenic dibromide, nor does the action of iodine on its sodium derivative result in the condensation of 2 molecules; an iodophenylmalonate appears to be formed instead.

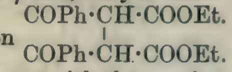
With allylic iodide, ethylic sodio-phenylmalonate yields *ethylic phenylallylmalonate*, which boils at 176—178° under 16 mm. pressure. When this is hydrolysed, only a small quantity of *phenylallylmalonic acid* is formed; this acid melts at 145° with evolution of carbonic anhydride, and its *calcium salt* crystallises with $\frac{1}{2}H_2O$. The main product of the hydrolysis is *phenylallylacetic acid*, which melts at 34°, and boils at 260° under the ordinary pressure, at 159—160° under 25 mm.; this acid, when heated with bromine, yields no additive product, but a *monobromo*-substitution *derivative*, melting at 75°. It does not undergo molecular transformation when boiled with sodium hydroxide. C. F. B.

Tautomerism. By LUDWIG KNORR (*Annalen*, 1896, **293**, 70—120. Compare Abstr., 1894, i, 360; also Wislicenus, Abstr., 1896, i, 552, and Claisen, Abstr., 1896, i, 557).—Ethylic dibenzoylsuccinate has been hitherto obtained in three forms: (1) with an "enolic" structure, having the constitution  $\begin{matrix}HO\cdot CPh\!:\!C\cdot COOEt\\ |\\ HO\cdot CPh\!:\!C\cdot COOEt\end{matrix}$, and called the *a*-salt, or ethylic bisphenylhydroxyacrylate; (2) the inactive ketonic form, of high melting point, prepared by von Baeyer and Perkin, and having the constitution



$$\begin{matrix}COOEt\cdot CH\cdot COPh\\ |\\ COPh\cdot CH\cdot COOEt\end{matrix} \qquad \begin{matrix}COPh\cdot CH\cdot COOEt\\ |\\ COOEt\cdot CH\cdot COPh,\end{matrix}$$

this corresponds with racemic acid, and is called the β-salt, or ethylic paradibenzoylsuccinate, and there remains (3) the inactive ketonic form of low melting point, which is known as the γ-salt, ethylic meso- or anti-dibenzoylsuccinate, and has the constitution



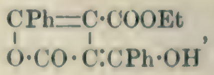
$$\begin{array}{l}\mathrm{COPh{\cdot}CH{\cdot}COOEt.}\\ \qquad\quad |\\ \mathrm{COPh{\cdot}CH{\cdot}COOEt.}\end{array}$$

The properties of these three isomerides are in harmony with the requirements of van't Hoff's theory, the β- and γ-salts differing from one another in physical characteristics, the former being less readily fusible and soluble than the latter, whilst they behave chemically as one compound, and both yield the quinonoïd derivative, $C_{18}H_{10}O_4$ (Abstr., 1894, i, 376) when heated at 270—290°; moreover, each yields with phenylhydrazine bisdiphenylpyrazolone (*loc. cit.*), and sodium ethoxide converts both into the α-salt. The latter, on the other hand, differs in both physical and chemical properties from the β- and γ-salts. It is a liquid with strongly acid action on litmus, and dissolves readily in soda, the solid salts being neutral, whilst ferric chloride develops a dirty-brown coloration; under the influence of heat the α-salt is converted into a mixture of the β- and γ-salts.

The action of iodine on the sodium derivative of ethylic benzoylacetate yields a mixture of the β- and γ-salts, which are separated by fractional crystallisation from alcohol. When an acetic acid solution of the β-salt is heated with ammonium acetate, diethylic 2 : 5 -diphenylpyrroline-3 : 4-dicarboxylate is formed, and in the same solvent, a molecular proportion of acetic acid gives rise to bisdiphenylpyrazolone and diethylic 1-phenylamido-2 : 5-diphenylpyrroline-3 : 4-dicarboxylate, the former alone being produced in alcoholic solution. Aqueous alkalis attack the β-salt with difficulty, but in alcoholic solution it is immediately converted into the alkali derivative of the α-salt, from which carbonic anhydride liberates a mixture of the β- and γ-salts; partial conversion into the α-salt takes place when it is heated during a few minutes at 170°. The γ-salt is also transformed into the enolic form when heated at 150—160°, and with sodium ethoxide likewise yields the sodium derivative of the α-salt.

Ethylic bisphenylhydroxyacrylate, the α-salt, or enolic form of ethylic dibenzoylsuccinate, is obtained most conveniently by treating a solution of the β- or γ-salt in alcohol with an alcoholic solution of sodium ethoxide; the liquid becomes intensely yellow, and rapidly deposits the *sodium* derivative as a bright yellow, crystalline powder. It is a viscous oil, having the colour of chlorine, and after remaining 5—6 hours at the ordinary temperature has undergone partial conversion into a mixture of β- and γ-salts, a transformation which is rapidly completed at 130°. This change also occurs when the substance is dissolved in absolute or dilute alcohol, but the α-salt is stable in benzene and ethereal solutions, and in its relation to the dissociating power of solvents resembles the substances described by Wislicenus and Claisen (*loc. cit.*).

The *lactone* of hydrogen ethylic dibenzoylsuccinate,

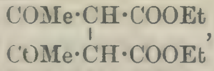


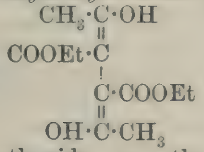
$$\begin{array}{l}\mathrm{CPh{=}C{\cdot}COOEt}\\ \;|\qquad\;\; |\\ \mathrm{O{\cdot}CO{\cdot}C{:}CPh{\cdot}OH}\end{array},$$

is obtained under certain conditions which are not yet fully understood, by the partial hydrolysis of the α-salt with sodium ethoxide; it crystallises from petroleum in yellow, transparent, rhombic prisms, and melts at 64—68°. The substance is strongly acidic, develops a bluish-green colouration with ferric chloride, and when heated at 270—290° yields the quinonoïd compound, $C_{18}H_{10}O_4$; a solution of the sodium derivative has reducing properties, and in general behaviour the lactone resembles ethylic isocarbopyrotritarate (Abstr., 1894, i, 360) to which it is analogous.

Investigation of the ethylic diacetylsuccinates has yielded results which correspond with the observations recorded above; the salts occur in three isomeric forms, which are referred to as α-, β, and γ salts.

The β-salt, when heated during 5 minutes at 81°, sinters to some extent, and undergoes partial conversion into the enolic form, and when very slowly heated will melt at 87°, the melting point being 89—90° when the temperature is raised rapidly; hence the stability limit of the salt is below the melting point, whereas the ketonic forms of ethylic dibenzoylsuccinate remain stable until a temperature much higher than the melting point is reached.

Ethylic antidiacetylsuccinate (*γ-salt*),  $\begin{array}{c}\mathrm{COMe\cdot CH\cdot COOEt}\\ | \\ \mathrm{COMe\cdot CH\cdot COOEt}\end{array}$, is produced along with the β-salt when the α-salt is kept at the ordinary temperature during several hours, or is heated above 60°; it melts at 68°, and the stability limit coincides with the melting point. In chemical behaviour, it resembles the β-salt, and, like that substance, is converted into the α-salt under the influence of sodium ethoxide or on application of heat.

Ethylic bishydroxycrotonate (α-salt), the enolic form of ethylic diacetylsuccinate,  $\begin{array}{l}\mathrm{CH_3\cdot C\cdot OH}\\ \quad\;\| \\ \mathrm{COOEt\cdot C}\\ \qquad\quad | \\ \qquad\quad\mathrm{C\cdot COOEt}\\ \qquad\quad \| \\ \mathrm{OH\cdot C\cdot CH_3}\end{array}$, is obtained by the action of alcoholic sodium ethoxide on the β-salt dissolved in alcohol; it is strongly acidic, and develops an intense claret-red coloration with ferric chloride. The salt is excessively unstable, and yields a mixture of the ketonic forms if kept at the ordinary temperature, the same change being effected rapidly at 60°; in alcoholic solution it also undergoes conversion into the β- and γ-salts, remaining, however, unchanged when dissolved in ether or benzene. The conversion of the α-salt into ethylic isocarbopyrotritarate or isocarbopyrotritaric acid on hydrolysis (*loc. cit.*), the production of furfuran derivatives under the influence of concentrated acids, and the formation of ethylic dimethylpyrrolinecarboxylate by the action of ammonia, are all phenomena which accord with the configuration represented above.

The striking parallel between the author's results and those of Wislicenus and Claisen have not led him to exactly the same conclusions; whilst they, for instance, regard α-dibenzoylacetylmethane (Abstr., 1896, i, 558), a substance which is converted into the β-modification at 80—90°, as stable above 110°, because that temperature is the stability limit of the β-salt, he looks on it as a tautomeric compound, implying by this expression a mixture of isomeric substances existing above the stability limit of any single component.

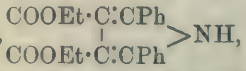
[With Julius Schmidt]—Corresponding with the isomeric forms of ethylic diacetylsuccinate, the acid itself occurs in three modifications, the production of which has already been described (compare Knorr and Haber (Abstr., 1894, i, 361).

α-Diacetylsuccinic acid corresponds with the foregoing α-salt, but, owing to its unstable character, has not been obtained in the free state; its lactone, however, is the isocarbopyrotritaric acid of Knorr and Haber.

β Diacetylsuccinic acid arises from the γ-acid or hydrogen ethylic γ-diacetylsuccinate under the influence of concentrated sulphuric or hydrochloric acid at 170°; it crystallises from water in transparent, colourless cubes, and melts and decomposes at 185—186°.

γ-Diacetylsuccinic acid is the substance melting at 160° which has been hitherto described as the α-acid (*loc. cit.*); the *phenylhydrazine* salt contains 2 mols. of the base, and the *silver* salt is an amorphous substance which rapidly decomposes. The *hydrogen ethylic* salt crystallises from a mixture of ether and alcohol in white, lustrous leaflets, and melts and decomposes at 150—152°.

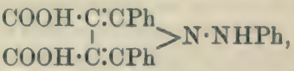
Ethylic 2:5-*diphenylpyrroline*-3:4-*dicarboxylate*,



$$\begin{matrix}\text{COOEt}\cdot\text{C:CPh}\\ |\\ \text{COOEt}\cdot\text{C:CPh}\end{matrix}\!>\!\text{NH},$$

is obtained by the action of ammonia on the ethylic salts of β-and γ-dibenzoylsuccinic acids; it crystallises from alcohol in transparent prisms, and melts at 151—152°. Phenylhydrazine converts the salts into bisdiphenylpyrazolone (Abstr., 1894, i, 376) and *ethylic* 1-anilido-2:5-diphenylpyrroline-3:4-dicarboxylate, which crystallises from glacial acetic acid in white, lustrous leaflets, and melts at 184—185°; cold, concentrated sulphuric acid forms a reddish-brown solution, which becomes deep red when heated, but this substance and the foregoing salt do not give the fir-splint reaction.

1-*Anilido*-2:5 *diphenylpyrroline*-3:4-*dicarboxylic acid*,



$$\begin{matrix}\text{COOH}\cdot\text{C:CPh}\\ |\\ \text{COOH}\cdot\text{C:CPh}\end{matrix}\!>\!\text{N}\cdot\text{NHPh},$$

is obtained on hydrolysis, and separates from dilute alcohol in small, white crystals containing $1H_2O$, which melt and vigorously decompose at 154°; it does not give the fir-splint reaction, and when heated liberates carbonic anhydride, forming a sublimate of yellowish red crystals, most probably consisting of anilidodiphenylpyrroline.

The double anhydride of dibenzoylsuccinic acid, $C_{18}H_{10}O_4$, is the quinonoid substance, described by Knorr and Scheidt, obtained on heating the ethylic β- and γ-salts; when heated with concentrated aqueous ammonia at 100°, it yields the *compound* $C_{18}H_{13}NO_4$, which crystallises from alcohol in yellow, rhombic prisms, and melts and decomposes at 202—203°. When the gas generated by nitric acid and arsenious anhydride is passed into a solution of the quinone in acetic acid, the *compound* $C_{18}H_{10}O_4,2HNO_2$ is produced, and separates in white, transparent prisms, containing $1\frac{1}{2}$ mol. of the solvent; at 60°, this substance evolves oxides of nitrogen, and acetic acid, the residue consisting of the original quinone. The same additive compound is formed when the action proceeds in ethereal solution, but after further treatment with the gas, effervescence occurs, and rapidly becomes vigorous; as this ceases, benzoylpyruvic acid separates in yellowish-white prisms, melting at 159—161°.

The *anhydride* of hydrogen ethylic dibenzoylsuccinate, $C_{22}H_{16}O_5$, constitutes the intermediate product in the formation of the quinone and crystallises from amylic alcohol in yellowish-white rhombohedra, which darken at 190°, and melt at 198—200°, evolving gas; it dissolves sparingly in the usual solvents, and exhibits green fluorescence. The substance is insoluble in cold alkalis, but dissolves slowly when heated; it forms a deep, purple-red solution with concentrated sulphuric acid, and is converted into the quinone if heated to 280°.

M. O. F.

Action of Alkali on Benzsulphydroxamic Acid [Benzenesulphonylhydroxylamide]. By EDWARD DIVERS (*Ber.*, 1896, **29**, 2324. Compare Piloty, Abstr., 1896, i, 555).—A claim for priority in a method for the preparation of hyponitrites. (Compare Trans., 1889, 767).

J. F. T.

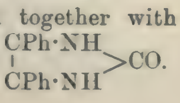
Action of Acid Amides on Benzoin. By ALFRED NEWLIN SEAL. (*J. Amer. Chem. Soc.*, 1896, **18**, 101—119).—The author has heated alcoholic solutions of various acid amides with benzoin in sealed tubes, and finds that the amide is in all cases decomposed by the alcohol, yielding the ethylic salt of the corresponding acid and ammonia, the latter then reacts with the benzoin, yielding tetraphenylazine, $C_4N_2Ph_4$; benzoinam, $C_{28}H_{24}N_2O$; benzoinidam, $C_{28}H_{23}NO_2$, and lophine, $C_3N_2HPh_3$. Compare Japp and Wilson, Japp and Burton, (Trans., 1886, **49**, 825, 843; 1887, **51**, 98). Similar results were obtained on heating the amides with benzoin in the absence of alcohol.

All attempts to prepare bromo- and chloro-derivatives of tetraphenylazine proved unsuccessful. Braun and Meyer's tetranitrotetraphenylazine (*Ber.*, 1888, **21**, 1269), when reduced with tin and hydrochloric acid, yields a yellow, amorphous *tetramido*-derivative which darkens when heated, and melts above 260°, at the same time undergoing decomposition. Its *hydrochloride* does not crystallise, but on evaporation of its aqueous solution in a vacuum, it is deposited as a reddish-brown, transparent mass. It melts at about 140° and is readily soluble in water. The *platinochloride*,

$$C_4N_2(C_6H_4NH_2HCl)_4,PtCl_4 + 11H_2O,$$

forms a reddish-brown precipitate. The crystallographic properties of tetraphenylazine are given in detail.

Carbamide and benzoin, when heated together with alcohol at 175—195°, yield diphenylacetylenureïn,



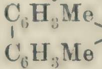
$\begin{array}{l}CPh\cdot NH\\ \mid\\ CPh\cdot NH\end{array}\!\!>\!CO$. (Compare Abstr., 1895, i, 304.)

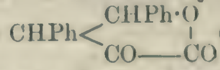
J. J. S.

The Aluminium Chloride Reaction. By MORIZ FREUND (*Monatsh.*, 1896, 395—400).—In preparing orthonitrodiphenylmethane by the action of aluminium chloride on a mixture of orthonitrobenzylic chloride and benzene, a resinous bye-product is obtained in which occur the hydrochlorides of two bases; a vigorous action appears to be conducive to their production. One of these is present in small quantity, and crystallises in colourless needles; it yields a *base*, also in the form of colourless needles, melting at 185—190°.

The second *substance* crystallises in yellow needles and is decomposed by boiling water, with production of the free *base* $C_{13}H_9NO$. This separates from dilute alcohol in beautiful, bright-yellow, glistening needles, and melts at 169°; it does not give the reactions characteristic of primary amines. When subjected to the action of nitrous acid, the base yields a yellow *compound* which does not melt below 350° and dissolves in dilute potash, giving a dark red solution similar to that produced by the oxyfluorenone of Graebe and Schestakow. (Compare Abstr., 1895, i, 372); when reduced in ethereal solution by means of zinc, the yellow compound yields a substance which, after distillation and crystallisation from dilute alcohol, melts at 168—172° and gives a reddish-brown precipitate when its aqueous solution is mixed with one of picric acid. The above base is not identical with acridone, phenanthridone or orthoamidofluorenone which have the same composition.

When a mixture of benzene and nitrobenzene is heated with aluminium chloride on the water bath Heusler's paramidodiphenyl was obtained; the yield was 8·5 per cent. of the weight of nitrobenzene employed. A. L.

Ditolylimide. By HERMANN SEYBERTH (*Ber.*, 1896, 29, 2594).—This substance,  $\begin{matrix}C_6H_3Me\\ | \\ C_6H_3Me\end{matrix}\!>\!NH$, is formed to some extent when orthotoluidine vapour is passed through a heated glass tube packed with fragments of pumice. It forms crystals with a yellowish-green surface lustre, and its solution in hot alcohol has a greenish fluorescence; it melts at 364° (uncorr.), and exhibits many of the reactions of carbazole. C. F. B.

Formation of Desylacetic Acid from Phenylpyruvic Acid and Benzaldehyde. By EMIL ERLENMEYER, jun. (*Ber.*, 1896, 29, 2585—2588).—The oxylactone  $CHPh\!<\!\begin{matrix}CHPh\cdot O\\ \quad | \\ CO\text{——}CO\end{matrix}$ (Abstr., 1894, i, 592), when reduced by boiling with zinc dust and acetic acid, yields the zinc salt of an unsaturated acetylmonhydroxy-acid, which, when boiled with hydrochloric acid, yields desylacetic acid,

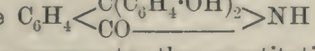
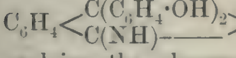
$\rightarrow OAc\cdot CHPh\cdot CHPh\cdot CH(OH)\cdot COOH \rightarrow OAc\cdot CPh{:}CPh\cdot CH_2\cdot COOH$
$\rightarrow OH\cdot CPh{:}CPh\cdot CH_2\cdot COOH \qquad \rightarrow COPh\cdot CHPh\cdot CH_2\cdot COOH$

Desylacetic acid really crystallises in tetragonal octahedra ($a : c = 1 : 0{\cdot}9374$), although the crystals have the appearance of regular octahedra. C. F. B.

Phthaleïn Derivatives. By JOSEF HERZIG and HANS MEYER (*Monatsh.*, 1896, **17**, 429—441).—Dimethylphenolphthaleïn, prepared by the action of methylic iodide on a solution of phenolphthaleïn in absolute alcohol, forms white, shining leaflets, and melts at 97—99°; it is insoluble in dilute alkalis, but is attacked by boiling, strong alcoholic potash, and the product, after separation from alcohol, is readily soluble in water, but yields the original compound on the addition of acids. This behaviour is not in accordance with the supposition that the substance is a lactonic salt. The compound cannot be benzoylated, and is precipitated from its solution in sulphuric acid on adding water; it is reduced, however, by zinc in alkaline solution, and the product melts at 144—146°, and has all the characteristics of a dimethoxytriphenymethanecarboxylic acid (compare Baeyer, Abstr., 1880, 650, and 1896, i, 564).

The authors have not succeeded in preparing lactonic diethoxyfluoresceïn; the monethoxy-compound, however, they find to act as a quinonoïd compound on etherification, and as a lactone on bromination, no compound resembling eosin being produced in the latter instance.

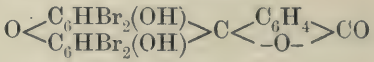
Monethylic fluoresceïncarboxylate yields a quinonoïd *acetyl* derivative, $C_{20}H_{10}O_5EtAc$, which crystallises in yellow needles, melting at 189—190°.

As the authors have already pointed out (Abstr., 1896, i, 237), the formation of an amido-compound on reducing the oxime of phenolphthaleïn militates against Friedländer's formula for the latter substance; they have repeated his experiments and confirmed his results. The product of reduction, $C_{20}H_{17}NO_3 + EtOH$, melts at 253—257°, dissolves in potash, is precipitated by carbonic anhydride, and yields a *diacetyl* derivative, $C_{20}H_{15}NO_3Ac_2$, which crystallises from alcohol in white needles melting at 205—208°; this substance is not identical with Errara and Gasparini's phenolphthalimide (Abstr., 1894, 294), but this fact does not exclude the possibility of it being an isomeride. Errari and Gasparini assign to their substance the structure  $C_6H_4{<}\begin{matrix}C(C_6H_4\cdot OH)_2\\ CO\text{———————}\end{matrix}{>}NH$; it is more probable, however, that this represents the constitution of Friedländer's compound, and that the other has the asymmetric formula  $C_6H_4{<}\begin{matrix}C(C_6H_4\cdot OH)_2\\ C(NH)\text{———}\end{matrix}{>}O$; the first formula has the advantage that it explains the observation, made by Friedländer, that the "oxime" suffers decomposition into parahydroxyorthobenzoylbenzoic acid and paramidophenol.

The authors advance further reasons for discarding the old "oxime" formula, and point out that a substance having the constitution $COOH\cdot C_6H_4\cdot C(C_6H_4\cdot OH):C_6H_4:NOH$ should yield either a monacetyl or a diacetyl compound, soluble in alkali; the compound in question, however, yields at least three substances on acetylation, none of which are soluble in alkalis. A. L.

The Phthaleïn-group. II. Fluoresceïn. By RICHARD E. MEYER and HEINRICH MEYER (*Ber.*, 1896, **29**, 2623—2626).—Baeyer has shown (this Journal, 1877, i, 195) that dihydroxybenzoylbenzoic acid, when heated at its melting point, yields phthalic anhydride and fluoresceïn. The authors find that a similar change takes place when dibromodihydroxybenzoylbenzoic acid is heated at 230—240°, phthalic anhydride and eosin being produced; the change is most readily effected when 20 per cent. of zinc chloride is introduced and the operation conducted in a stream of hydrogen.

The production of eosin from dibromodihydroxybenzoylbenzoic acid in the manner described above makes it appear certain that the former substance has the symmetrical structure:



$$O<\begin{matrix}C_6HBr_2(OH)\\C_6HBr_2(OH)\end{matrix}>C<\begin{matrix}C_6H_4\\-O-\end{matrix}>CO$$

[$O:Br_2:OH:C = 6:5:3:4:1$ in each ring.]

The product obtained on melting dibromodihydroxybenzoylbenzoic acid contains a considerable proportion (about 56 per cent.) of a red substance, which, on reduction and reoxidation, yields fluoresceïn.

A. L.

The Phthaleïn-group. III. Orcinolphthaleïns. By RICHARD E. MEYER and HEINRICH MEYER (*Ber.*, 1896, **29**, 2627—2640).—The crude product obtained by heating orcinol with phthalic anhydride in presence of a condensing agent (compare Fischer, this Journal, 1877, i, 205) consists of three substances of the phthaleïn type, to which the authors refer as α-, β-, and γ-orcinolphthaleïn respectively.

α-Orcinolphthaleïn is obtained from the mixture by extraction with cold dilute alkalis, which leave it undissolved; it separates from acetic acid in colourless crystals. It dissolves in strong alkalis with production of a bluish-red coloration, but is only sparingly soluble in dilute soda and ammonia; its properties are those of a very weak acid, but it is extracted from its alkaline solution by means of ether. On adding alcoholic potash to an alcoholic solution of the phthaleïn, the *potassium* salt separates in the form of blue needles, having a bronze-like lustre. α-Orcinolphthaleïn yields the additive compound with hydrogen chloride described by Fischer (*loc. cit.*), but could not be made to form the monacetyl derivative obtained by him; the latter is doubtless the compound, described later, obtained from β-orcinolphthaleïn. The *dibenzoyl* derivative, $C_{22}H_{14}O_5Bz_2$, which is formed on shaking the alkaline solution of the phthaleïn with benzoic chloride, is not dissolved by cold alkali, but is slowly hydrolysed by hot alcoholic potash; it dissolves readily in chloroform, and hot benzene, is sparingly soluble in methylic alcohol, ethylic alcohol and acetone, but is insoluble in light petroleum; it crystallises from alcohol, on the addition of benzene, in the form of colourless crystals melting at 284—285°.

Tetrabrom-α-orcinolphthaleïn, $C_{22}H_{12}Br_4O_5$, is formed on adding bromine to a solution of α-orcinolphthaleïn in glacial acetic acid; it crystallises from hot nitrobenzene in yellowish prisms, and dissolves in aqueous soda, the resulting solution having a violet colour which is changed to an intense blue by heat.

α-Orcinolphthaleïn is easily reduced in alkaline solution by means of zinc dust, the corresponding *α-orcinolphthalin*, $C_{22}H_{18}O_5$, being produced. The latter forms thick quadratic crystals, which fall to pieces at 130°, water being eliminated; it melts with effervescence at 256°, reversion to the corresponding phthaleïn occurring simultaneously; the latter change is most readily effected when the hot alkaline solution of the phthalin is oxidised with potassium ferricyanide. An *acetyl* compound, $C_{24}H_{18}O_5$, is obtained when the foregoing phthalin is heated with acetic anhydride; it separates from alcohol in thick rhombohedra, melting at 219°, is insoluble in alkalis but is gradually hydrolysed when boiled with them.

β-Orcinolphthaleïn, $C_{22}H_{16}O_5 + \frac{1}{2}H_2O$, constitutes the portion of the above crude product which is soluble in ammonia but is precipitated from this solution on exposure to the atmosphere. It crystallises in microscopic bundles of needles or large, six-sided, orange tables. The properties and analyses of the substance are in agreement with those of the "monacetylorcinolphthaleïn" described by Fischer, and the two substances are doubtless identical. It dissolves readily in ethylic and methylic alcohols and ethylic acetate, yielding brown solutions, and is sparingly soluble in hot water, benzene, and acetic acid. Aqueous solutions of alkalis, alkali carbonates or ammonia dissolve it, and yield solutions of a cherry-red colour, which is not destroyed by dilution; the addition of acid, however, causes the reprecipitation of the phthaleïn. Hydrochloric acid combines directly with the substance with production of a compound similar to that obtained from the α-phthaleïn. It is reduced by soda and zinc dust to the corresponding *phthalin*, which dissolves sparingly in hot benzene, and separates in crystals on cooling; on cautious oxidation, it is reconverted into the original phthaleïn.

Diacetyl-β-orcinolphthaleïn, $C_{22}H_{14}O_5Ac_2$, forms bundles of yellow needles, melting at 227—228°. *Dibenzoyl-β-orcinolphthaleïn*,

$$C_{22}H_{14}O_5Bz_2,$$

forms colourless, shining crystals, and melts at 244—245°.

Tetrabromo-β-orcinolphthaleïn, $C_{22}H_{12}Br_4O_5$, crystallises in colourless shining tables; it dissolves in alkali carbonates with production of a greenish-black solution, which, on dilution, becomes a dirty red. This is doubtless the tetrabromorcinolphthaleïn actually isolated by Fischer, as its properties are in complete accordance with those of that substance. It is reduced to the β-phthalin by zinc dust and caustic potash.

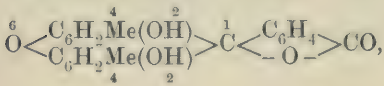
γ-Orcinolphthaleïn, $C_{22}H_{16}O_5$ is obtained from the crude mixture of phthaleïns by the action of gaseous ammonia, followed by dissolution in water; the solution, on exposure to the atmosphere, deposits the β-phthaleïn, the filtered liquid yielding the γ-compound when acidified with sulphuric acid. When its ammoniacal solution is mixed with alcohol and sulphuric acid, and then evaporated, the substance separates in pale yellow prisms, whilst a concentrated solution in acetic acid deposits dark orange crystals.

γ-Orcinolphthaleïn dissolves in alcohol, forming a brown solution, from which it is deposited in bundles of bright yellow, short needles. It bears a strong resemblance to fluoresceïn; when precipitated in the amorphous state it is yellow, whilst its solutions in ammonia, alkalis, or their carbonates are brown, and show a greenish fluorescence weaker than that of fluoresceïn; it acts as a dye, imparting a yellowish hue to silk. It dissolves in warm sodium acetate or phosphate, forming solutions which exhibit a fluorescence not affected on extracting the liquids with ether; it is also somewhat soluble in hydrochloric and dilute sulphuric acids. Its solution in ether is not fluorescent. It is reduced by zinc-dust and soda, with production of the colourless phthalin, which readily suffers reoxidation on treatment with potassium permanganate.

Diacetyl-γ-orcinolphthaleïn, $C_{22}H_{12}O_5Ac_2$, melts at 207—208°, and crystallises in colourless prisms.

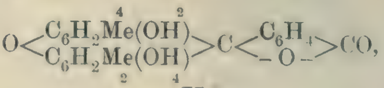
Tetrabromo-γ-orcinolphthaleïn, $C_{22}H_{14}Br_4O_5$, crystallises in flat, truncated, brownish prisms. It is very sparingly soluble in all the ordinary media; it dissolves in alkalis and alkali carbonates, forming intense eosin-red solutions without fluorescence, but which are yellowish-red by reflected, and a rose-colour by transmitted light. Gaseous ammonia imparts a rose colour to the compound, which is finally transformed into the ammonium salt, a substance having a green metallic lustre; it dyes silk a beautiful eosin-red. When it is heated with sodium hydroxide, a deep blue solution is obtained, which contains two substances, one soluble in water and having an odour reminiscent of bromophenol, the other insoluble in water and precipitated by acids. It is completely reduced in alkaline solution with sodium amalgam, the phthalin thus formed being very readily oxidised to a coloured, fluorescent substance.

The three foregoing orcinolphthaleïns are doubtless constituted in the manner indicated by the formulæ,



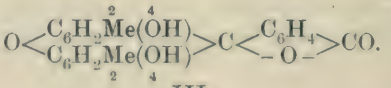
$$\overset{6}{O}<\begin{matrix}C_6H_2\overset{4}{Me}(O\overset{2}{H})\\C_6H_2\underset{4}{Me}(O\underset{2}{H})\end{matrix}>\overset{1}{C}<\begin{matrix}C_6H_4\\-O-\end{matrix}>CO,$$

I.



$$O<\begin{matrix}C_6H_2\overset{4}{Me}(O\overset{2}{H})\\C_6H_2\underset{2}{Me}(O\underset{4}{H})\end{matrix}>C<\begin{matrix}C_6H_4\\-O-\end{matrix}>CO,$$

II



$$O<\begin{matrix}C_6H_2\overset{2}{Me}(\overset{4}{O}H)\\C_6H_2\underset{2}{Me}(\underset{4}{O}H)\end{matrix}>C<\begin{matrix}C_6H_4\\-O-\end{matrix}>CO.$$

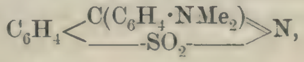
III

Of these formulæ, III undoubtedly represents the fluorescent γ-orcinolphthaleïn. A. L.

Patent-blue Colouring Matters; derivatives of Benzylsultone, Benzylsultame, and Benzylidenesultime. By Paul Fritsch (*Ber.*, 1896, 29, 2290—2301).—"*Pseudosaccharin*" *chloride*, $C_6H_4<\begin{matrix}CCl\\SO_2\end{matrix}>N$, was obtained by Jesurun (Abstr., 1893, i, 716) in crystals which melt at 143—145°; repeated crystallisation from benzene has raised the melting point to 149°.

Phenylbenzylidenesultime, $C_6H_4<\begin{matrix}CPh\\SO_2\end{matrix}>N$, is the substance obtained by Remsen and Saunders on treating orthobenzoylbenzenesulphonic chloride with ammonia (Abstr., 1895, i, 475); the author has prepared it by heating the foregoing chloride with benzene and aluminium chloride, and it crystallises in lustrous, rhombic plates, melting at 164°. The same action gives rise to *diphenylbenzylsultame*, $C_6H_4<\genfrac{}{}{0pt}{}{CPh_2}{SO_2}>NH$, which crystallises in prisms, and melts at 210°; the *potassium* derivative crystallises in long, colourless needles.

Dimethylparamidophenylbenzylidenesultime,



$$C_6H_4<\genfrac{}{}{0pt}{}{C(C_6H_4\cdot NMe_2)}{\text{——}SO_2\text{——}}>N,$$

is produced when "pseudosaccharin" chloride is heated with dimethylaniline and aluminium chloride; it crystallises from toluene in colourless leaflets, and melts at 221°.

The author confirms the views of Remsen and Saunders (*loc. cit.*) regarding the isomeric chlorides of orthosulphobenzoic acid, and the paper also contains a description of the preparation of tetramethylparatriamidotriphenylmethaneorthosulphonic acid from tetramethyldiamidobenzhydrol and metamidobenzenesulphonic acid. M. O. F.

Triphenylethanone [Diphenylacetophenone]. By A. COLLET (*Bull. Soc. Chim.*, 1896, [3], **15**, 22—23).—Trichloracetic chloride, when heated with benzene, gives diphenylacetophenone, $CHPh_2\cdot COPh$ (Delacre, Abstr., 1896, i, 485), whilst chloracetic chloride, under similar conditions, gives phenylacetophenone (phenyl benzyl ketone). It was therefore of interest to ascertain what the dichlor-acid would give. A mixture of dichloracetic chloride, benzene, and aluminium chloride, when heated for 10 hours on a water bath, yields diphenylacetophenone. M. W. T.

Dyes of the Pyronine Group. By JOACHIM BIEHRINGER (*J. pr. Chem.*, 1896 [2], **54**, 217—258. Compare Abstr., 1895, i, 146).—Metadiethylamidophenol melts at 78°, not at 74° (*loc. cit.*); its *hydrochloride*, $C_{10}H_{15}NO,HCl + \frac{1}{2}H_2O$, was prepared. Tetramethyldiamidodihydroxydiphenylmethane melts at 178°, not at 175° (Abstr., 1895, i, 47); the hydrochloride of its benzoyl derivative, $C_{17}H_{20}N_2O_2Bz_2,2HCl$, melts at 72—73°, not at 141° (Abstr., 1895, i, 147).

Tetraethyldiamidodihydroxydiphenylmethane, $CH_2[C_6H_3(OH)\cdot NEt_2]_2$, is prepared by dissolving metadiethylamidophenol (11 grams) in wood spirit (25 c.c.), adding fuming hydrochloric acid (3 c.c.), cooling and mixing with formaldehyde (2·5 c.c. of a 40 per cent. solution); after a time, crystallised sodium acetate (4·5 grams) dissolved in twice its weight of wood spirit is added, and the solution is slowly evaporated. It crystallises in prisms, melts at 168°, and dissolves in hot alcohol and xylene, but only sparingly in hot acetone.

The *sulphate*, $C_{21}H_{30}N_2O_2,H_2SO_4$, was prepared. Details of the production of tetramethyldiamidodiphenylmethane oxide (*loc. cit.*) by the action of sulphuric acid on the dihydroxy-base are given, together with prescriptions for oxidising the oxide to the colouring matter, known as pyronine, both by chloranil and by sodium nitrite. Pyronine *dihydrochloride*, $C_{17}H_{20}N_2OCl_2 + H_2O$, crystallises in flat prisms with a blue lustre when the pyronine is dissolved in 20 per cent. hydrochloric acid and the solution is evaporated; when dried in a xylene bath, until constant in weight, it passes into the green *hydrochloride*, $C_{17}H_{21}N_2OCl + \frac{1}{2}H_2O(?)$. The *platinochloride*,

$$(C_{17}H_{20}N_2O)_2,H_2PtCl_6,$$

crystallises in prisms with a green lustre.

Tetramethyldiamidoxanthone, $CO{:}[C_6H_3(NMe_2)]_2{:}O$, is the compound previously mentioned (*loc. cit*) as obtainable from the anhydro-base by the prolonged action of sulphuric acid. It is an oxidation product, and is formed in small quantity in most of the reactions of the group of dyes under consideration; thus, treatment of pyronine with potassium ferricyanide in alkaline solution yields a crude mass from which the xanthone may be extracted by appropriate solvents to the extent of about 10 per cent. of the pyronine. It crystallises from alcohol in yellowish prisms with oblique ends, or in aggregates of needles, melts at 240—242°, and dissolves in hot wood spirit, alcohol, acetone, chloroform, ethylic acetate, carbon bisulphide and benzene, "sparingly in hot ligroin and hardly at all in petroleum-benzin." The solutions in the first three of these solvents and also that in strong sulphuric acid show a blue fluorescence; this fact, together with the yellow colour of the crystals, leads to the conclusion that the compound is a xanthone derivative. The blue fluorescence passes to green in dilute acid solutions. The *hydrochloride*, $C_{17}H_{18}N_2O_2,HCl$, and the *platinochloride* are described, also a *tribromo*-derivative, $C_{17}H_{15}Br_3N_2O_2$, obtained by direct bromination in a glacial acetic acid solution.

To prove the constitution of pyronine, tetramethyldiamidodiphenylmethane was nitrated to the dinitro-derivative of melting point 190—191° (Abstr., 1895, i, 98), this was reduced to the tetramido-compound (*loc. cit.*), the orientation of which was diagnosed by the fact that when heated in a sealed tube at 140° with hydrochloric acid and subsequently oxidised by air or ferric chloride, it yields *tetramethyldiamidoacridine*, $CH{<}\begin{smallmatrix}C_6H_3(NMe_2)\\ C_6H_3(NMe_2)\end{smallmatrix}{>}N$ (see below). The formation of this compound shows that there are two amido-groups in tetramethyltetramidodiphenylmethane which are both in the ortho-position relatively to the methylene group. This orientation having been settled, it only remained to convert the tetramido-compound into the dihydroxy-derivative by means of the diazo-reaction; the compound thus produced $[CH_2{:}OH{:}NMe_2 = 1{:}2{:}4]$, was proved to be identical with the condensation product of formaldehyde and dimethylmetamidophenol. It follows from this that the oxygen in the anhydro-base formed by oxidising the dihydroxy-derivative joins two ortho-positions in the two benzene nuclei, and that the colour base of pyronine is a carbinol of the form $OH{\cdot}CH{<}\begin{smallmatrix}C_6H_3(NMe_2)\\ C_6H_3(NMe_2)\end{smallmatrix}{>}O$, which passes into the dye $CH{<}\begin{smallmatrix}C_6H_3\text{---}(NMe_2)\\ C_6H_3({:}NMe_2Cl)\end{smallmatrix}{>}O$. The formation of the xanthone from the carbinol is self-evident.

Tetramethyldiamidoacridine (see above) crystallises in yellow needles, melts at 181—182°, and dissolves in water, alcohol, acetone, and hot benzene; in strong sulphuric acid it gives a yellow solution with a blue fluorescence. The *hydrochloride* and *platinochloride* are described.

The condensation of benzaldehyde with metadimethylamidophenol, producing rosamine, is discussed. The compound primarily formed is an orthodihydroxyleuco-malachite green (m. p. 176°), which readily undergoes intramolecular dehydration, yielding an anhydride of the pyronine class, capable of similar oxidation to a dye, which, however, is a sulphonic salt. A. G. B.

Ketones derived from Naphthalene. By L. Rousset (*Bull. Soc. Chim.* [3], **15**, 58—72).—By the addition of an equivalent of an acid chloride in small quantities to a boiling solution of naphthalene in carbon bisulphide with aluminium chloride, the author obtains a fair yield of a mixture of the α- and β-substituted naphthalenes of the formula $R{\cdot}CO{\cdot}C_{10}H_7$. In some cases, the two isomerides can be separated by direct crystallisation, but it is, as a rule, more advantageous to first obtain the compounds which the ketones form with picric acid, $R{\cdot}CO{\cdot}C_{10}H_7,C_6H_2(NO_2)_3{\cdot}OH$, which differ more widely in their solubilities in alcohol than the ketones themselves. These picrates are easily decomposed by means of sodium carbonate into sodium picrate and the ketone. The α- and β-ketones yield α- and β-naphthoic acids on oxidation with nitric acid.

α-Naphthyl methyl ketone, an almost colourless liquid, has a sp. gr. = 1·1336 at 0°, boils at 295—296°, and is soluble in organic solvents. Its oxime melts at 135—136°, and its picrate melts at 116°, and is very insoluble in alcohol.

β-Naphthyl methyl ketone forms white needles; melts at 51°, boils at 171—172° under 11 mm. pressure, and is not very soluble in alcohol and light petroleum, Its *oxime* melts at 142—143°, and its *picrate* is very soluble in alcohol.

α-Naphthyl ethyl ketone is a liquid boiling at 166—168° under 8 mm. pressure; it is insoluble in water and only slightly soluble in cold light petroleum, soluble in chloroform, alcohol, &c. The *oxime* is crystalline, and melts at 57—58°; the *picrate* melts at 77—78°, and is very insoluble in alcohol.

β-Naphthyl ethyl ketone is a crystalline substance melting at 56—57°, and boiling under atmospheric pressure at 312—314°; it is slightly soluble in cold, light petroleum or alcohol. The *oxime* melts at 133°.

α-Naphthyl propyl ketone is a liquid of sp. gr. = 1·0861 at 0°; it boils under atmospheric pressure at 316—318°, and is soluble in organic solvents. The *oxime* is a liquid, boiling at 206—208° under 13 mm. pressure. The *picrate* is soluble in alcohol.

β-Naphthyl propyl ketone, a solid very difficult to free from alcohol, melts at 50—51°, boils at 322—324°, and is soluble in alcohol. The *oxime* melts at 89°. The *picrate* is almost insoluble in alcohol.

α-Naphthyl isopropyl ketone is a liquid of sp. gr. = 1·0761 at 0° which boils at 308—310° under atmospheric pressure, and is soluble in organic solvents. The *oxime* is a solid, melting at 140°, or after fusion at 125°. The *picrate* melts at 66—67°, and is very insoluble in alcohol.

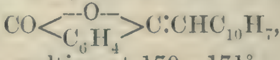
β-Naphthyl isopropyl ketone, a liquid of sp. gr. = 1·0617 at 0°; it boils at 312—314°, and is soluble in organic solvents. The *oxime* melts at 121—122° and boils at 200—203° under 12 mm. pressure.

α-Naphthyl isobutyl ketone, a liquid of sp. gr. = 1·059 at 0°, boils at 319—321° under atmospheric pressure, and at 180—182° at 9 mm. pressure. The *oxime* is a viscous liquid, boiling at 200—205° at 10 mm. pressure. The *picrate* is soluble in alcohol.

β-Naphthyl isobutyl ketone, a liquid of sp. gr. = 1·050 at 0°; boils at 323—325°, and is soluble in organic solvents. The *oxime* melts at 99°, and boils at 208—210° at 10 mm. pressure. The *picrate* is only slightly soluble in alcohol.

The naphthyl phenyl ketones are easily separated by treating the mixture of picrates with benzene, in which the β-derivative is very insoluble; it melts at 82°, and its picrate melts at 112—113.°

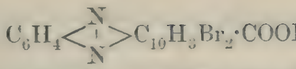
M. W. T.

β-Naphthylacetic Acid. By Oscar Blank (*Ber.*, 1896, **29**, 2373—2375.)—*β-Naphthylacetonitrile*, $C_{10}H_7{\cdot}CH_2{\cdot}CN$, may be prepared in the usual way from the corresponding chloride, and crystallises in white, spherical masses, melting at 79—81°. *β-Naphthylacetic acid* separates from hot water in irregular, nacreous crystals, melting at 137·5—139°. The *silver* salt crystallises in lustrous plates, and the *methylic* salt is a thick, light yellow oil. The acid is converted into an ethereal salt when it is simply heated with an alcohol. When distilled, it decomposes into β-methylnaphthalene and carbonic anhydride. It reacts with phthalic anhydride and sodium acetate to form *β-naphthylmethylenephthalide*,  $CO{<}\substack{-O-\\ C_6H_4}{>}C{:}CHC_{10}H_7$, which crystallises in golden yellow needles, melting at 170—171°.

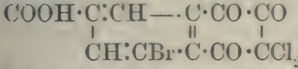
A. H.

Action of Nitric Acid on Bromoprotocatechuic Acid; Conversion into 3 : 4′-Dibromo-β-naphthaquinone-2′-carboxylic Acid. By E. C. Theodor Zincke, Bruno Francke [and in part, Max Schmidt], (*Annalen*, 1896, **293**, 120—175. Compare Abstr., 1896, i, 308).—3 : 4′-*Dibromo-β-naphthaquinone-2′-carboxylic acid*, obtained by the cautious oxidation of bromoprotocatechuic acid in small quantities by dilute nitric acid, crystallises from glacial acetic acid in dark red needles, which melt at 253—254°, and contain 1 mol. of the solvent; it is very readily soluble in acetone, less easily in alcohol and hot glacial acetic acid, and only sparingly in ether, chloroform and benzene. The *sodium* salt is sparingly soluble, and the red colour of the solution slowly changes to brownish green.

3 : 4′-*Dibromo-β-naphthaquinol-2′-carboxylic acid* is formed when the quinone is reduced with stannous chloride in acetic acid, and crystallises from hot acetic acid in yellowish aggregates; concentrated nitric acid regenerates the quinone, and both chlorine and caustic soda convert the quinol into the same compounds as its oxidation product. The *diacetyl* derivative crystallises from glacial acetic acid in colourless leaflets, and melts at 239°.

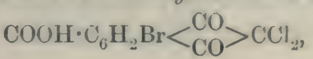
Dibromonaphthazinecarboxylic acid,  $C_6H_4<\overset{N}{\underset{N}{|}}>C_{10}H_3Br_2\cdot COOH$, is obtained by the action of orthophenylenediamine on dibromonaphthaquinonecarboxylic acid dissolved in glacial acetic acid; it dissolves sparingly in the usual solvents, and forms an intense yellow solution in concentrated nitric acid, whilst concentrated sulphuric acid develops a dark violet coloration.

3:4′:2-*Dibromhydroxy-a-naphthaquinone-2′-carboxylic acid* is produced by treating the quinone or quinol with dilute caustic soda, the lactone of 4-α-bromo-β-hydroxypropionyl-5-bromisophthalic acid (see below) being formed at the same time; it separates from glacial acetic acid in small needles containing 1 mol. of the solvent, and decomposes evolving gas at 281°. The *sodium* and *ammonium* salts are dark red, and sparingly soluble; the *eurhodole*, obtained from orthophenylenediamine, crystallises in slender, red needles, and forms sparingly soluble, red, alkali salts. Oxidation of the acid with potassium permanganate gives rise to bromomellithic acid, and chlorine converts it into chlorodibromo- and dichlorobromo-triketonaphthalenecarboxylic acid, according to the conditions observed.

3:3:4′-*Dichlorobromo*-1:2:4-*triketohydronaphthalene-2′-carboxylic acid*,

$$\begin{array}{l}COOH\cdot C\colon CH-\cdot C\cdot CO\cdot CO\\ \qquad\quad CH\colon CBr\cdot C\cdot CO\cdot CCl_2\end{array}$$
, H_2O, is obtained by suspending chlorobromohydroxynaphthaquinonecarboxylic acid in chloroform, and passing chlorine into the liquid; it contains 1 mol. H_2O, even after recrystallisation from a mixture of ether and light petroleum, separating in colourless needles, which char and evolve gas at 200°. Stannous chloride converts the triketo-compound into 3:4:2-chlorobromhydroxy-α-naphthaquinonecarboxylic acid, the substance from which it was obtained; this acid will be described subsequently.

2′:2′:4-*Dichlorobromo*-1′-*hydroxy*-3′-*ketohydrindene*-2:1′-*dicarboxylic acid*, $COOH\cdot C_6H_2Br<\frac{C(OH)(COOH)}{CO}>CCl_2$, is produced with great readiness when water acts on the foregoing acid, and is obtained by acidifying an alkaline solution of that substance; it crystallises from hydrochloric acid in four-sided plates containing $3H_2O$, which is removed at 100°, and the anhydrous substance chars and liberates gas at 215°. When crystallised from nitric acid of sp. gr. = 1·4, it contains $1H_2O$, and melts with vigorous effervescence at 160°, subsequently charring at 200°. The aqueous solution gradually becomes red, and yields an amorphous, red precipitate, owing to elimination of hydrogen chloride; in consequence of this change, which proceeds rapidly with boiling water, it is necessary to crystallise the substance from mineral acids. The *dimethylic* salt crystallises from benzene, and melts at 168—169°; it dissolves at once in caustic soda, and develops a red coloration. The acid is indifferent towards boiling, concentrated nitric acid, but is oxidised by chromic acid to the corresponding keto-compound, and finally yields bromotrimellithic acid.

2′:2′:4-*Dichlorobromo*-1′:3′-*diketohydrindene-2-carboxylic acid*,

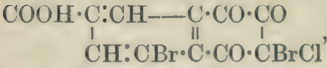


$$COOH\cdot C_6H_2Br<\substack{CO\\CO}>CCl_2,$$

is obtained by the action of aqueous chromic acid solution on the foregoing compound, and is almost insoluble in ether, light petroleum, benzene, and concentrated hydrochloric and nitric acids; it crystallises from alcohol, and becomes red and effervesces at 280°. Sodium carbonate dissolves the substance with development of a red colour, and hydrochloric acid precipitates from the solution 4-*dichloraceto*-5-*bromisophthalic acid*, which crystallises from nitric acid of sp. gr. = 1·4, and melts evolving gas at 226—227°; alkalis eliminate chlorine from the substance, which is indifferent towards oxidising agents. 4-*Trichloraceto*-5-*bromisophthalic acid* is obtained by digesting the indene derivative with a solution of bleaching powder, and after some hours acidifying the liquid with hydrochloric acid; it dissolves with difficulty in water, dilute acids, benzene, and chloroform, and crystallises from nitric acid in small octahedra, sintering at 220°, and melting at 235°. The *dimethylic* salt is crystalline and melts at 169°.

5-*Bromotrimellithic acid* may be obtained from any of the foregoing substances by the action of potassium permanganate or chromic acid, chlorobromo- or dibromo-hydroxynaphthaquinonecarboxylic acid being the most convenient source; it separates from nitric acid of sp. gr. = 1·4 in minute crystals, and melts at 237°. The *dimethylic* salt crystallises from water in long, slender needles, and melts at 130—131°; the *trimethylic* salt crystallises from methylic alcohol in aggregates of small needles, and melts at 110°.

3:3:4′-*Chlorodibromo*-1:2:4-*triketohydronaphthalene*-2′-*carboxylic acid*,

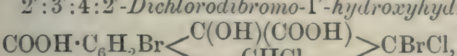
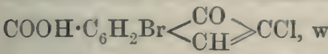
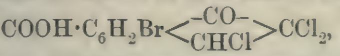


$$\begin{array}{l} COOH\cdot C{:}CH\text{——}C\cdot CO\cdot CO \\ \qquad\quad | \qquad\qquad \| \qquad\; | \\ \qquad\quad CH{:}CBr\cdot C\cdot CO\cdot CBrCl \end{array},H_2O,$$

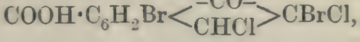
is obtained along with the dichlorobromo-acid when chlorine acts on dibromhydroxynaphthaquinonecarboxylic acid suspended in chloroform; it becomes yellow and sinters at 160°, melting at 253°. It is readily converted into chlorobromhydroxyhydrindenecarboxylic acid, which is formed on crystallising it from dilute mineral acids; hot glacial acetic acid gives rise to chlorobromhydroxynaphthaquinonecarboxylic acid, but this change also involves the production of hydroxyindenecarboxylic acid.

3:4:3:4′-*Dichlorodibromo*-1:2-*diketohydronaphthalene*-2′-*carboxylic acid* is produced when chlorine acts on dibromo-β-naphthaquinonecarboxylic acid suspended in glacial acetic acid; it is also formed from the quinone, and when the latter is used, chloroform may be employed instead of acetic acid. It crystallises from glacial acetic acid on the addition of concentrated hydrochloric acid, and separates from nitric acid of sp. gr. = 1·4 in rosettes of small needles, containing $1H_2O$, which is removed above 100°; it melts and slowly decomposes at 150°. Water and a solution of sodium acetate dissolve the substance without change if gently heated, but decomposition occurs on boiling the liquid; caustic soda and sodium carbonate hydrolyse the diketone forming dichlorodibromo-1′-hydroxyhydrindene-2:1′-dicarboxylic acid (see below). The diketone is indifferent towards oxidising agents, but stannous chloride reduces it to 3:4′-chlorobromo-β-naphthaquinone-2′-carboxylic acid, which rapidly passes into the quinol; more energetic action converts it into 4′-bromo-1:2-naphthaquinone-2′-carboxylic acid. When the substance is heated at 175—180°, it reddens, and liberates halogen, yielding chlorobromo-β-naphthaquinonecarboxylic acid.

3:4′-*Chlorobromo-2-hydroxy-α-naphthaquinone-2′-carboxylic acid* is obtained from the foregoing diketone by dissolving it in hot, glacial acetic acid, adding an equal volume of concentrated sulphuric acid, and gently heating the liquid; it is also produced by the action of very dilute caustic soda on chlorobromo-β-naphthaquinonecarboxylic acid or its quinol. It separates from glacial acetic acid in pale yellow crystals containing 1 mol. of the solvent, and does not melt below 290°, although it sinters at this temperature; the *sodium* salt is sparingly soluble, and crystallises in beautiful, red needles.

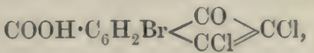
2′:3′:4:2′-*Dichlorodibromo-1′-hydroxyhydrindene-2:1′-dicarboxylic acid*,  $\mathrm{COOH\cdot C_6H_2Br}<\begin{smallmatrix}\mathrm{C(OH)(COOH)}\\ \mathrm{CHCl}\end{smallmatrix}>\mathrm{CBrCl}$, is obtained, as stated above, by the action of sodium carbonate on 3:4:3:4′-dichlorodibromo-1:2-diketohydronaphthalene-2′-carboxylic acid, and is sparingly soluble in alcohol, ether, acetic acid, and chloroform; it crystallises from a mixture of glacial acetic and concentrated hydrochloric acids in thin plates, and melts, decomposing, at 242°. When treated with boiling water, carbonic anhydride is eliminated, and the substance is converted into 2′:4-*chlorobromo-1′-ketohydrindene-2-carboxylic acid*,  $\mathrm{COOH\cdot C_6H_2Br}<\begin{smallmatrix}\mathrm{CO}\\ \mathrm{CH}\end{smallmatrix}>\mathrm{CCl}$, which crystallises from dilute acetic acid in elongated, yellow leaflets, and gradually chars at 250°; chlorine converts it into 2′:2′:3′-*trichloro-4-bromo-1′-ketohydrindene-2-carboxylic acid*,  $\mathrm{COOH\cdot C_6H_2Br}<\begin{smallmatrix}\mathrm{-CO-}\\ \mathrm{CHCl}\end{smallmatrix}>\mathrm{CCl_2}$, which crystallises from nitric acid of sp. gr. = 1·4 in colourless leaflets, and melts at 230°.

2′:3′:4:2′-*Dichlorodibromo-1′-ketohydrindene-2-carboxylic acid*,



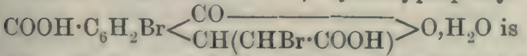
$$\mathrm{COOH\cdot C_6H_2Br}<\begin{smallmatrix}\mathrm{-CO-}\\ \mathrm{CHCl}\end{smallmatrix}>\mathrm{CBrCl},$$

is produced when the foregoing hydroxycarboxylic acid is dissolved in hot glacial acetic acid and oxidised with chromic acid; it crystallises from nitric acid in slender needles, and melts at 205—206°. 2′:3′:4-*Dichlorobromo-1′-ketoindene-2-carboxylic acid*,

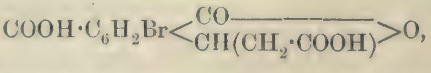


$$\mathrm{COOH\cdot C_6H_2Br}<\begin{smallmatrix}\mathrm{CO}\\ \mathrm{CCl}\end{smallmatrix}>\mathrm{CCl},$$

is obtained by treating it with excess of sodium carbonate, and acidifying the yellow solution with hydrochloric acid; the yellow *sodium* salt is sparingly soluble, and the *anilide* is red.

The *lactone* of 4-α-bromo-β-hydroxypropionyl-5-bromisophthalic acid,  $\mathrm{COOH\cdot C_6H_2Br}<\begin{smallmatrix}\mathrm{CO}\\ \mathrm{CH(CHBr\cdot COOH)}\end{smallmatrix}>\mathrm{O,H_2O}$ is produced along with dibromhydroxynaphthaquinonecarboxylic acid by the action of alkali on dibromo-β-naphthaquinonecarboxylic acid; it crystallises from nitric and dilute hydrochloric acids in lustrous leaflets, melts and decomposes at 224°, above which temperature it solidifies, and finally fuses about 280°. Although indifferent towards acidic oxidising agents, it is converted into bromotrimellitic acid by potassium permanganate or a solution of bleaching powder. The *dimethylic* salt crystallises from methylic alcohol in colourless prisms, and melts at 168°.

The *lactone* of 4-β-hydroxypropionyl-5-bromisophthalic acid,



$$COOH\cdot C_6H_2Br<\begin{matrix}CO\text{———————}\\CH(CH_2\cdot COOH)\end{matrix}>O,$$

is obtained by heating the foregoing substance with hydriodic acid and red phosphorus for 1½ hour at 160°; it crystallises from nitric acid in small, colourless needles, and melts at 275—276°. The *barium* salt forms slender needles, containing $3H_2O$; the *dimethylic* salt crystallises in leaflets, and melts at 102°.

Asymmetric propionylisophthalic acid is obtained by reducing bromhydroxypropionylbromisophthalic acid in aqueous solution with 4 per cent. sodium amalgam, and separates from glacial acetic or nitric acid in colourless crystals melting at 265—266°.

4-*Acetyl-5-bromisophthalic acid* is produced when the lactone of bromhydroxypropionylbromisophthalic acid is heated with very dilute aqueous barium hydroxide; it crystallises from water, and melts at 224—225°. The *dimethylic* salt crystallises from methylic alcohol in rosettes of small needles, and melts at 114—115°.

Asymmetric ethylisophthalic acid is obtained by the prolonged action of sodium amalgam on acetobromisophthalic acid, and crystallises from hot water; it becomes brown and melts at 266—267°.

M. O. F.

A Correction [Diamidonaphthalenesulphonic Acids]. By PAUL FRIEDLÄNDER and W. H. KIELBASINSKI (*Ber.*, 1896, **29**, 2574).—In the preparation of the two naphthylenediaminedisulphonic acids [1 : 3′ : 4 : 1′] and [1 : 3′ : 3 : 1′] from 1 : 3′-naphthylenediamine, the formulæ were exchanged through an error, so that for the compound [1 : 3′ : 4 : 1′], the compound [1 : 3′ : 3 : 1′] should be read, and *vice versâ*.

Further, it is now stated that the naphthalene-1 : 4′-disulphonic acid is readily isolated by means of its sodium salt which is sparingly soluble in a solution of sodium chloride.

J. F. T.

Essence of Angelica archangelica. By FELICE GIORDANI (*Gazzetta*, 1896, **26**, ii, 315—326). The essential oil of angelica (*Angelica archangelica*) is a limpid, heavy, reddish liquid of neutral reaction, which slowly deposits crystals consisting of a *substance*, $C_{32}H_{62}O_5$; the crystals are broad, yellow scales, melting at 74—77°. After fractionally distilling the oil under reduced pressure, a solid residue remains in the flask which, when washed with ether and crystallised from hot alcohol, yields a neutral *substance* of the empirical composition $C_7H_{13}O$; it forms small, white crystals, melting at 68—70°.

The distillate from the oil, when hydrolysed with alcoholic potash and distilled in a current of steam, yields a terpene-like oil, boiling at 240—270°, and evidently a mixture; the residue in the distilling flasks contains the potassium salts of methylethylacetic acid and of a *hydroxypentadecylic acid*, $C_{15}H_{30}O_3$. The latter acid, when purified by crystallisation from petroleum, is obtained in aggregates of minute needles melting at 84°; its *barium* salt $(C_{15}H_{29}O_3)_2Ba$, forms a heavy, white precipitate. The acid readily yields an *acetyl* derivative, $C_{15}H_{29}O_3Ac$, which crystallises in pearly scales, melting at 59°.

Bromopentadecylic acid, $C_{15}H_{29}BrO_2$, is prepared by heating the hydroxy-acid at 100° with hydrobromic acid; it crystallises in minute pearly scales, melting at 65°. *Iodopentadecylic acid*, $C_{15}H_{29}IO_2$, obtained by heating the hydroxy-acid at 160° with hydriodic acid, is similar to the preceding acid in appearance and melts at 78—79°.

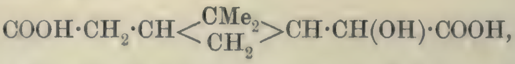
Hydroxypentadecylic acid is not present in the free state in the essence, but as an alkylic salt; traces of a phenolic substance were also found in the oil. W. J. P.

Ethereal Oils. Palmarosa Oil. By EDUARD GILDEMEISTER and KARL STEPHAN (*Arch. Pharm.*, 1896, **234**, 321—330).—This oil, formerly known as Turkish geranium oil, is prepared in the province of Bombay by distilling with water the leaves of a grass, *Andropogon Schoenanthus, L.* The sp. gr. of the purer samples examined varied between 0·888 and 0·896, and their rotation (in a 100 mm. tube) between +1°40′ and −1°55′. They were all soluble in three times their weight of 70 per cent. (by volume) alcohol, and this solubility affords a convenient means of detecting impurities, many of which are insoluble in alcohol of this strength. The commonest impurity is at present paraffin—of five samples from the London Docks all contained this substance, two of them to the extent of 50 and 90 per cent. respectively. The purer oil contains 1 per cent. of dipentene, with perhaps a trace of methylheptenone; also 12—20 per cent. of ethereal salts of acetic and normal caproic acids. The alcohol of these salts is, no doubt, geraniol, as this is the only alcohol that has hitherto been detected in the oil under examination. C. F. B.

Orientation in the Terpene Series: Pinene. By ADOLF VON BAEYER (*Ber.*, 1896, **29**, 2775—2796. Compare Abstr., 1896, i, 245, 308, and 620.)—The α-oxime of pinonic acid has been already described (Abstr., 1896, i, 246), and is an inactive substance which melts at 150°; it is prepared from α-pinonic acid, the solid product of oxidation of pinene, and the syrupy mother liquor from which α-pinonic acid has been separated, when treated with hydroxylamine yields two oximes, isomeric with the first. Of these the β-oxime, which melts at 128°, is identical with the substance obtained by Tiemann and Semmler from their liquid pinonic acid (Abstr., 1895, i, 478); it is dextrorotatory, and 1 decimetre of an 8·2 per cent. solution in ether has $\alpha = 2°18'$. The *γ-oxime* is less readily soluble than the β-modification, and separates from glacial acetic acid as a microcrystalline powder, melting at 190°—191°; it is lævo-rotatory in almost the same degree as the β-oxime is dextrogyrate, and 1 decimetre of a 2·8 per cent. solution in methylic alcohol has $\alpha = 47·5'$.

Pinarin, $C_{10}H_{14}O_3$, is slowly deposited in crystals from that fraction of the neutral product of oxidation of pinene which boils at 150—180° under a pressure of 15 mm.; it crystallises from hot petroleum in concentric aggregates of long needles melting at 66—68°, and has the properties of a lactone.

Hydroxyhomopinic acid,



$$\mathrm{COOH{\cdot}CH_2{\cdot}CH}<\begin{matrix}\mathrm{CMe_2}\\ \mathrm{CH_2}\end{matrix}>\mathrm{CH{\cdot}CH(OH){\cdot}COOH},$$

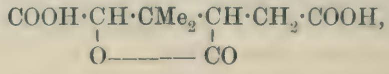
is obtained by reducing an alkaline solution of pinoylformic acid (Abstr., 1896, i, 621) with sodium amalgam; it crystallises from water in rhombic leaflets, and melts at 130°—133°. The *silver* salt is a crystalline powder which dissolves readily in water; the *copper* salt is bright blue.

α *Ketoisocamphoronic acid* (*dimethyltricarballoylformic acid*),

$$\mathrm{COOH{\cdot}CO{\cdot}CMe_2{\cdot}CH(COOH){\cdot}CH_2{\cdot}COOH},$$

is produced when sodium hypochlorite or hypobromite acts on pinoylformic acid; it crystallises from water in six and eight-sided plates and leaflets, and melts, evolving gas, at 186—187°. The *silver* salt crystallises from water in minute needles; copper acetate produces no insoluble salt, and on heating the liquid cuprous oxide is precipitated. When the aqueous solution is heated with lead peroxide, dimethyltricarballylic acid is produced; the anhydro-acid melts at 145—146°, and when treated with boiling water yields dimethyltricarballylic acid melting at 149—151°, a specimen which had been heated with water at 230° melting at 156—157° (compare Tiemann and Semmler, Abstr., 1895, i, 478).

When α-ketoisocamphoronic acid is reduced with sodium amalgam, the *lactone* of α-hydroxyisocamphoronic acid,



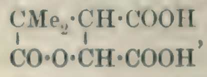
$$\begin{array}{l}\mathrm{COOH{\cdot}CH{\cdot}CMe_2{\cdot}CH{\cdot}CH_2{\cdot}COOH,}\\ \qquad\quad |\qquad\qquad\ \ |\\ \qquad\quad \mathrm{O}\text{———}\mathrm{CO}\end{array}$$

is formed; it crystallises from water in thick prisms containing $1H_2O$, and sinters at 160°, solidifying as the temperature rises, and finally melting at 185—186°. On heating the lactone with hydriodic acid during 4 hours at 170°, it is converted into isocamphoronic acid, which therefore has the constitution

$$\mathrm{COOH{\cdot}CH_2{\cdot}CMe_2{\cdot}CH(COOH){\cdot}CH_2{\cdot}COOH},$$

an expression which does not agree with the formula of Bredt and Tiemann.

The *lactone* of α-hydroxydimethyltricarballylic acid,



$$\begin{array}{l}\mathrm{CMe_2{\cdot}CH{\cdot}COOH}\\ |\qquad\ \ |\\ \mathrm{CO{\cdot}O{\cdot}CH{\cdot}COOH}\end{array},$$

is obtained by brominating dimethyltricarballylic acid with phosphorus tribromide and bromine, and allowing the product to fall into boiling water; it separates from ethylic acetate in very large crystals, and melts at 196° when slowly heated, and at 207° when the temperature is raised rapidly, much gas being evolved. The *calcium* salt crystallises in needles containing $3H_2O$, and when dried at 125° contains $1H_2O$; the *barium* salt is similar, and the *silver* salt crystallises in short needles. Fusion of the lactonic acid with potash gives rise to oxalic and *as*-dimethylsuccinic acids.

Valuable theoretical conclusions are drawn from the foregoing observations and those already recorded. Wagner's formula for pinene is still supported, and the breaking down of a molecule having this structure is traced through its various phases, represented by the production of pinonic, pinoylformic, pinic, and norpic acids. The last-named substance, $COOH\cdot CH\Big<\begin{matrix}CMe_2\\CH_2\end{matrix}\Big>CH\cdot COOH$, is a derivative of the dimethylated tetramethylene residue, which the author calls the picean-ring. M. O. F.

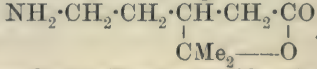
Orientation in the Terpene Series: Caronic Acid. By Adolf von Baeyer and Wladimir Ipatieff (*Ber.*, 1896, **29**, 2796—2802).—In view of the stability of the trimethylene-ring towards alkaline permanganate, carone, which according to von Baeyer has the constitution, $\begin{array}{l}CHMe\cdot CO\cdot CH\\ \vert\qquad\qquad\;\; \vert\\ CH_2-CH_2\cdot CH\end{array}\!\!>CMe_2$ (Abstr., 1896, i, 246), has been submitted to oxidation with this agent; caronic acid, a dimethyltrimethylene-1 : 2-dicarboxylic acid, capable of existing in *cis*- and *trans*-modifications, has been thus obtained.

The *caronic acids*, $CMe_2\Big<\begin{array}{l}CH\cdot COOH\\ \vert\\ CH\cdot COOH\end{array}$, are produced when carone is heated in a reflux apparatus on the water bath with potassium permanganate for 36 hours; after removing oxalic acid, the neutral liquid is extracted with ether, acidified, and again extracted, the acid syrup obtained in this manner depositing the *cis*-acid in crystals, the *trans*-modification being isolated by conversion into the ammonium salt.

cis-*Caronic acid* (cis-*dimethytrimethylene*-1 : 2-*dicarboxylic acid*) crystallises from water in plates, and melts at 174—175°; it is almost soluble in chloroform, and dissolves but sparingly in ether and petroleum. The *ammonium* salt is precipitated in needles on adding ether to the alcoholic solution; the *calcium* and *silver* salts are amorphous. The *anhydride* is formed at the melting point of the acid, and after crystallisation from ether melts at 54—56°. When the acid is heated for 7 hours at 100° with a solution of hydrobromic acid saturated at 0°, it is converted completely into the isomeric terebic acid.

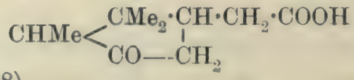
trans-*Caronic acid* crystallises from water in prisms, and melts at 212°, no gas being evolved below 245°; the *ammonium* salt crystallises from water in prisms, and the *silver* salt is sparingly soluble. This modification does not form an anhydride; it is converted into terebic acid under the same conditions as the *cis*-acid. M. O. F.

Methoethylheptanonolide melting at 64° (Homoterpenylic acid methyl ketone). By J. C. W. Ferdinand Tiemann (*Ber.*, 1896, **29**, 2616—2621).—The oxime of methoethylheptanonolide (Wallach, Abstr., 1895, i, 548) crystallises in rhombs, and melts at

79—80°; when heated with concentrated sulphuric acid at 100°, it is converted into acetic acid, along with the base *methyl-2-aminoethyl-3-pentolide*-2 : 5, 

$$\begin{array}{l}NH_2{\cdot}CH_2{\cdot}CH_2{\cdot}CH{\cdot}CH_2{\cdot}CO\\ \qquad\qquad\qquad CMe_2\text{——}O\end{array}$$

. This result establishes the formula for methoethylheptanonolide already put forward (*loc. cit.*); and although it apparently favours von Baeyer's formula for pinonic acid, the author continues to advocate the expression



$$CHMe<\begin{array}{l}CMe_2{\cdot}CH{\cdot}CH_2{\cdot}COOH\\ CO\text{——}CH_2\end{array}$$

(Abstr., 1895, i, 478). M. O. F.

Preparation of Terpenylic and Terebic Acids. By FRIEDRICH MAHLA and J. C. W. FERDINAND TIEMANN (*Ber.*, 1896, **29**, 2621—2622).—By oxidation with chromic and sulphuric acids, methoethylheptanonolide is converted without difficulty into terpenylic acid; when nitric acid is used as the oxidising agent, terebic acid is produced.

M. O. F.

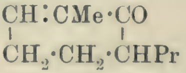
Menthene Nitrosochloride and some of its Derivatives. By W. O. RICHTMANN and EDWARD KREMERS (*Amer. Chem. J.*, 1896, **18**, 762—779).—Owing to the varying statements with regard to the melting point of menthene nitrosochloride (compare Abstr., 1892, 1479; 1894, i, 468; *Ber.*, **26**, 2561), the authors have been induced to make a thorough study of the physical constants of menthene and its nitrosochloride. The menthene was prepared by the dehydration of menthol by means of hydrogen potassium sulphate or anhydrous copper sulphate, followed by careful fractionation. A table is given showing the boiling points, densities and specific rotatory powers of the various fractions obtained. The nitrosochloride was prepared by the gradual addition of a solution of 18 c.c. of concentrated hydrochloric acid in an equal volume of glacial acetic acid to a mixture of 45 c.c. of menthene, 45 c.c. of glacial acetic acid and 33 c.c. of ethylic nitrite placed in a freezing mixture. The product was submitted to repeated fractional crystallisation, the melting points, sp. rotatory powers and percentage yields of the various fractions being recorded in several tables. The results show that the nitrosochloride prepared by the above method is a mixture, and indicate the existence of a dextrogyrate, a lævogyrate and an inactive compound. Very little of the lævo-compound could be obtained. Three specimens of the nitrosochloride having specific rotatory powers differing by 30° all yielded optically inactive benzylamine bases. On heating with alcoholic potash, the dextrogyrate nitrosochloride yielded a lævogyrate nitrosomenthene, melting at 66·5—67·5° after re-crystallisation from alcohol. An inactive nitrosomenthene (m. p. 65—67°) was obtained from the inactive nitrosochloride. Menthylamine nitrate was prepared by the reduction of nitrosomenthene with acetic acid and zinc dust, but the yield was very small. The ketone, $C_{10}H_{16}O$, prepared by the action of hydrochloric acid on nitrosomenthene, boils at 207—208° (not 210—212°, as stated by Kremers and Urban). The nitrosomenthene from the mixed nitrosochlorides yielded a slightly lævogyrate ketone, that from the inactive nitrosochloride a slightly dextrogyrate compound ($[\alpha]_D = -0{\cdot}3173°$ and $+0{\cdot}4299°$ respectively).

A crystalline *hydrosulphide* of the ketone was obtained, melting at 206—208°, which on analysis gave results nearly agreeing with the formula, $C_{10}H_{16}O,2H_2S$. By the application of Baeyer's method, a small quantity of the nitroso-derivative of the ketone was prepared, melting at 115—115·5°, but the yield was too small to admit of further work. A crystalline *hydrazone*, $C_{10}H_{16}\!:\!N_2HPh$, of the ketone was prepared, melting and evolving gas at 73·5—74°. It undergoes rapid decomposition in the air, gas being given off and a dark green, resinous mass remaining. When substituted phenylhydrazines were employed, no satisfactory results were obtained; negative results were also obtained in the attempt to prepare the nitrosochloride of the ketone. The reduction of the ketone by Beckmann's method was tried, when the chief products obtained were a yellow oil and a white, crystalline substance. The greater part of the oil boiled at 207—208°, and had sp. gr. = 0·9019 at 20° and $[\alpha]_D = -0{\cdot}8144°$. It therefore differed but slightly in its physical constants from the original ketone. A molecular refraction determination pointed to this oil being the alcohol $C_{10}H_{18}O$, but its chemical behaviour indicated that it consisted mainly of the unchanged ketone. The crystalline substance (m. p. 160—162°) gave analytical results which showed that it was neither the alcohol $C_{10}H_{18}O$ nor the corresponding pinacone. The investigation of these products will be continued. A. C. C.

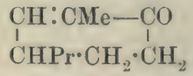
Substances derived from Camphoroxime and Fenchone-oxime. By FRIEDRICH MAHLA and J. C. W. FERDINAND TIEMANN (*Ber.*, 1896, **29**, 2807—2824. Compare Abstr., 1895, i, 426).—The paper contains a more detailed account of the salts of camphorimine; the nitrate melts at 158—159°, and the base, which sublimes at the ordinary temperature, melts at 95°. The *hydrochloride* crystallises in long needles, and sublimes without melting when heated; the *aurochloride* dissolves in ether.

Camphorimine becomes liquid when exposed to the air, and also under the influence of caustic alkalis, ammonia being eliminated; various agents resolve it into ammonia and camphor, this change taking place when the base is treated with boiling hydriodic acid. When distilled in an atmosphere of steam, the base passes over in the form of an oil, which boils at 104° under a pressure of 17 mm., yielding a mixture of the original base and a nitrile. An aqueous solution of the hydrochloride, if left for a considerable period, yields a feebly basic *compound*, $C_{30}H_{46}N_2$, which melts at 100°, and forms an *aurochloride*.

Camphenylnitramine, contrary to the statement of Angeli (Abstr., 1895, i, 426) gives Liebermann's reaction; the potassium derivative is in part converted into camphorimine under the influence of alcoholic potash. The authors lay down their reasons for ascribing to camphenylnitramine the nitramine formula, and confirm the observations of Angeli and Rimini (*loc. cit.*) regarding the action of strong sulphuric acid on the substance. Isocamphor, the product of this change, yields a *semicarbazone* melting at 215°, and the *bisnitrosochloride* melts at 120—121°. Reduction converts it into a dihydrogenised secondary alcohol, which is oxidised to *dihydroisocamphor*, a liquid boiling at 203°, the semicarbazone of which melts at 162°. Oxidation of isocamphor with potassium permanganate gives rise to a dibasic *acid*, $C_8H_{14}O_4$, which melts at 96°, and with acetic chloride yields the *anhydride*, melting at 60°. These results have led Angeli and Rimini to regard the acid as an isopropylglutaric acid, and they ascribe to isocamphor a constitution represented by one of the formulæ



$$\begin{array}{l}\mathrm{CH{:}CMe{\cdot}CO}\\ \mathrm{CH_2{\cdot}CH_2{\cdot}CHPr}\end{array}$$



$$\begin{array}{l}\mathrm{CH{:}CMe{-}CO}\\ \mathrm{CHPr{\cdot}CH_2{\cdot}CH_2}\end{array}$$

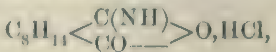
Fenchoneoxime melts at 163° (Wallach gives 148—149°), and when the ethereal solution is treated with nitrous acid, it yields the *nitrate* of fenchoneimine, $C_{10}H_{17}N,HNO_3$, which melts at 152°; the *hydrochloride* gives rise to fenchone when treated with sodium hydrogen sulphite. *Fenchonitrimine*, $C_{10}H_{16}N_2O_2$, corresponds with camphenylnitramine, and remains in the ethereal liquid after separation of fenchoneimine nitrate; it softens at 52°, and melts at 58°.

The paper concludes with some interesting theoretical observations.

M. O. F.

Camphoric Nitrile and Isomeric Change of Isonitrosocamphor. By GIUSEPPE ODDO and G. LEONARDI (*Gazzetta*, 1896, **26**, i, 405—423).—The substance which Oddo obtained by the action of acetic chloride on isonitrosocamphor (Abstr., 1893, i, 660) is found to be *camphoric β-mononitrile*, $CN{\cdot}C_8H_{14}{\cdot}COOH$, and owes its formation to an isomeric change of isonitrosocamphor; since the cyanogen radicle is attached to the methylene group contiguous to the ketonic carbon atom, the compound is termed a β-nitrile, in accordance with Claisen and Manasse's suggestion (Abstr., 1893, i, 479). It is also obtained on treating isonitrosocamphor with phosphorus pentachloride, phosphorus trichloride, or acetic anhydride; after evaporating the solvent, the residue is treated with water, dissolved in sodium carbonate, precipitated with hydrochloric acid, and crystallised from boiling water. It is colourless, melts at 151—152°, is soluble in alcohol, chloroform, ether or benzene, and is readily distinguished from its isomeride by giving a colourless solution in alkali, and by not yielding camphoquinone on treatment with sodium nitrite and acetic acid. The *silver* salt, $CN{\cdot}C_8H_{14}{\cdot}COOAg$, is a voluminous white powder, and is readily converted into the methylic salt, which crystallises in hard, transparent crystals, melting at 41—42°; the ethylic salt melts at 22—24°.

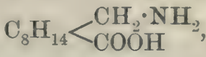
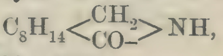
An ethereal solution of the nitrile absorbs dry hydrogen chloride yielding a white, crystalline hydrochloride, melting at 156—158°, identical with the α-camphorisoimide hydrochloride prepared by Hoogewerff and van Dorp (Abstr., 1896, i, 313) by the action of acetic chloride on β-camphoramic acid; the constitution,



$$\mathrm{C_8H_{14}}<\!\begin{array}{l}\mathrm{C(NH)}\\ \mathrm{CO}\text{———}\end{array}\!>\mathrm{O,HCl},$$

assigned to it by the Dutch chemists is in agreement with the fact that dry hydrogen chloride does not induce isomeric change in the methylic salt of the β-nitrile. The hydrochloride yields a *platinochloride*, $(C_{10}H_{15}NO_2)_2,H_2PtCl_6$, which crystallises in beautiful, yellow scales, and an *aurochloride*, which forms small, yellow crystals, melting at 130—140° ; the hydrochloride, platinochloride, and aurochloride are slowly decomposed by water, yielding β-camphoramic acid.

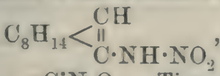
Camphoric β-nitrile is converted into a mixture of camphoric acid and camphorimide by heating with fuming hydrochloric acid, and into camphorimide by sulphuric acid.

The *hydrochloride* of β-amidocampholic acid,  $C_8H_{14}<\begin{matrix}CH_2\cdot NH_2\\ COOH\end{matrix}$, is formed on reducing the mononitrile in absolute alcoholic solution with sodium and, after dilution with absolute alcohol, passing in a current of dry hydrogen chloride ; after filtration, the filtrate is evaporated to dryness, and the residue crystallised from light petroleum ; it crystallises in white needles, melting and decomposing at 268—270°, and gives a *platinochloride*, $(C_{10}H_{19}NO_2)_2,H_2PtCl_6$, which crystallises in yellow scales blackening at 270°. On heating the hydrochloride above its melting point, it is converted into an anhydride,  $C_8H_{14}<\begin{matrix}CH_2\\ CO-\end{matrix}>NH$, which crystallises in colourless prisms melting at 228—230°.

The *anhydride*, $(CN\cdot C_8H_{14}\cdot CO)_2O$, of camphoric β-mononitrile is formed during the preparation of the mononitrile by the action of acetic anhydride or chloride on isonitroso-camphor, and is best prepared by treating a soda solution of the nitrile with acetic anhydride ; it crystallises in colourless, transparent prisms, melting at 172—173°, is soluble in chloroform or alcohol, and when boiled with alcoholic potash and acidified yields the original nitrile.

The conversion of isonitroso-camphor into camphorimide by the action of sulphuric acid (Angeli, Abstr., 1893, i, 277) proceeds in two stages ; β-camphoramic acid is first formed, and by the further action of sulphuric acid is converted into the imide. W. J. P.

NOTE BY ABSTRACTOR.—It should be noted that the β-derivatives mentioned in this paper are termed α-derivatives by Hoogewerff and van Dorp (*loc. cit.*).

Action of Nitrous Acid on Camphoroxime. By ANGELO ANGELI (*Gazzetta*, 1896, **26**, ii, 29—34. Compare Abstr., 1895, i, 426).—The author considers that pernitrosocamphor, $C_{10}H_{16}N_2O_2$, which is identical with Tiemann's camphenylnitramine, has not the constitution,  $C_8H_{14}<\begin{matrix}CH\\ \|\\ C\cdot NH\cdot NO_2\end{matrix}$, assigned to it by the latter, but contains the group $:C:N_2O_2$. Tiemann supposes the first action of nitrous acid on camphoroxime to be the formation of camphoroxime nitrite, which then spontaneously changes into the isomeric camphorimine nitrate ; this then loses water, giving camphenylnitramine or pernitrosocamphor.

A quantitative yield of pernitrosocamphor can be obtained by the action of nitrous acid on camphoroxime in very dilute solution ; further, it may be conveniently prepared by dissolving camphoroxime in amylic nitrite, when white needles of campherimine nitrite separate, leaving pernitrosocamphor in solution. On treating camphoroxime in sodium ethoxide solution with amylic nitrite, pernitrosocamphor is produced. These facts speak strongly against Tiemann's hypothesis respecting the formation of pernitrosocamphor, which requires the presence of free nitrous acid.

Campherimine nitrate should, according to Tiemann's view, readily yield an anhydride; but the author was unable to prepare such a compound, the nitrate crystallising unchanged from hot acetic anhydride. No nitric acid is obtained on treating the nitrate with concentrated sulphuric acid, although this reaction is characteristic of nitramines (Lachmann, "Ueber Nitroharnstoff, &c.," *Inaug. Diss. Munich*, 1895).

The yellow potassium salt of pernitrosocamphor melts at 43°, but on cautiously acidifying its aqueous solution and filtering, a yellow salt melting first at 57°, and after resolidification at 43°, is obtained; it differs from the salt melting at 43° by being readily soluble in dilute aqueous alkali. W. J. P.

Action of Nitrous Acid on Camphoroxime. By ANGELO ANGELI and ENRICO RIMINI (*Gazzetta*, 1896, **26**, ii, 34—45; 45—54. Compare preceding abstract).—The most convenient method of preparing camphoroxime consists in heating a mixture of camphor (175—200 grams), spirit (600 c.c.), hydroxylamine hydrochloride (100 grams) and caustic soda (140 grams) gradually on the water bath, then boiling for 4 hours, evaporating off most of the alcohol and pouring into water; after filtering off the deposited oxime, a further quantity can be obtained by exactly neutralising with hydrochloric acid.

Pernitrosocamphor (Abstr., 1895, i, 426) is best prepared by adding sodium nitrite to a solution of camphoroxime in dilute hydrochloric acid and recrystallising the deposited powder from alcohol; it crystallises in large, colourless crystals of characteristic odour, melts at 45°, and has the normal molecular weight in freezing benzene.

On treating it with concentrated sulphuric acid, pernitrosocamphor evolves nitric oxide, and on distilling the product in a current of steam, *isocamphor*, $C_{10}H_{16}O$, is obtained as an oil of pleasant odour, boiling at 216° under ordinary pressure with slight resinification; it slowly changes in the air, is resinified by alkalis, and immediately decolourises permanganate, but does not condense with benzaldehyde or ethylic formate. Its oxime melts at 106°, and is dissolved unaltered by concentrated sulphuric acid, but is readily hydrolysed by boiling with dilute sulphuric acid. Isocamphor, when treated with an alcoholic solution of semicarbazide acetate, yields a *semicarbazone*, melting at 215°.

Isocamphor bisnitrosochloride, $C_{10}H_{16}NO_2Cl$, is prepared by the action of acetic chloride on a mixture of isocamphor and amylic nitrite cooled in ice; it is deposited in small, white crystals, melting and decomposing at 120—121°, and its formation indicates that the isocamphor molecule contains a double bond.

On reducing isocamphor in alcoholic solution with sodium, distilling in a current of steam, and treating the oily product with permanganate to remove impurities, a *tetrahydroisocamphor* is obtained as a heavy, colourless oil having a lavender-like odour. Chromic acid mixture converts it into a *dihydroisocamphor* which is obtained as a colourless oil of fruity odour boiling at 203° ; its *semicarbazone*,

$$C_{10}H_{16}:N\cdot NH\cdot CO\cdot NH_2,$$

prepared by the aid of semicarbazide acetate, crystallises in thin, white needles melting at 162°, and when treated with dilute sulphuric acid yields pure dihydroisocamphor. The latter is stable towards permanganate, and does not condense with benzaldehyde, but gives a crystalline *compound* with sodium hydrogen sulphite.

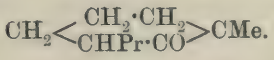
On oxidising isocamphor with alkaline permanganate, it yields a dibasic *acid*, $C_8H_{14}O_4$, which crystallises in white needles, melting at 96° ; determinations of its electrical conductivity give the values

$$K = 0{\cdot}00525 \text{ and } \mu\infty = 351,$$

which are characteristic of the glutaric acids. Its *anhydride*, $C_8H_{12}O_3$, formed on treating it with acetic chloride, crystallises in long, thin needles, melting at 60°. The acid of the composition, $C_8H_{14}O_4$, yields succinic acid when oxidised with a mixture of chromic and sulphuric acids, so that it most probably has the constitution

$$COOH\cdot CHPr\cdot CH_2\cdot CH_2\cdot COOH.$$

The most probable constitution at present assignable to isocamphor is the following



$$CH_2<\begin{matrix}CH_2\cdot CH_2\\ CHPr\cdot CO\end{matrix}>CMe.$$

Pernitrosocamphor is violently acted on by bromine, but on adding bromine to its glacial acetic acid solution saturated with dry hydrogen bromide, *bromopernitrosocamphor*, $C_{10}H_{15}BrN_2O_2$, slowly separates ; it crystallises in long, colourless, lustrous needles, melting at 114°, and when treated with dilute alcoholic potash is converted into *isobromopernitrosocamphor*, $C_{10}H_{15}BrN_2O_2$, which separates from alcohol or petroleum in large, colourless crystals, melting at 67°. Both isomerides give off nitric oxide and hydrogen bromide when treated with concentrated cooled sulphuric acid, the iso-compound yielding *isocamphenone*, $C_{10}H_{14}O$, which separates from petroleum in yellowish crystals of pleasant odour, melting at 92° ; it soon resinifies in the air, gives an *oxime* melting at 170°, and on reduction with alcohol and sodium seems to give tetrahydroisocamphor.

Dibromopernitrosocamphor, $C_{10}H_{14}Br_2N_2O_2$, may be prepared by treating a chloroform solution of pernitrosocamphenone with bromine ; it separates from petroleum in large, white crystals, melting at 133°.

On treating camphenone with hydrogen bromide in glacial acetic acid solution, a new *bromocamphor*, $C_{10}H_{15}BrO$, is obtained ; it is extremely stable towards acids, but is readily converted into camphenone by alkalis and yields camphenonoxime on treatment with alkaline hydroxylamine solution.

A new *dibromocamphor*, $C_{10}H_{14}Br_2O$, is obtained by treating camphenone with bromine in carbon bisulphide solution ; it separates from alcohol or petroleum in large, colourless crystals melting at 58—59°.

It may be readily distinguished from ordinary dibromocamphor by treating it with alcoholic potash, when *bromocamphenone*, $C_{10}H_{13}BrO$, is produced; it forms large, colourless crystals melting at 70°, and has the curious property that on cooling its hot saturated solutions, all the substance separating collects in one large crystal.

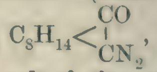
Provisional constitutional formulæ for camphenone and its derivatives are proposed.

In a note appended to this paper, Angeli combats Aschan's views (Struktur und stereochemischen Studien in der Camphergruppe, Helsingfors, 1895) as to the structure of camphenone and monoketazocamphadione, and also the view that camphor contains the group $CO\cdot CH_2\cdot CH\colon$ W. J. P.

Action of Nitrous Acid on Oximes of the Camphor Series. By ANGELO ANGELI and ENRICO RIMINI (*Gazzetta*, 1896, **26**, ii, 228—230).—The results which the authors have obtained by the action of nitrous acid on camphoroxime have led them to extend the investigation to other oximes of the camphor series (Abstr., 1895, i, 426).

They find that camphenonoxime is converted into pernitrosocamphenone by nitrous acid. Menthonoxime, when treated with nitrous acid, yields an unstable liquid product which is decomposed by concentrated sulphuric acid with evolution of gas.

Fenchonoxime is converted by nitrous acid into a beautiful *pernitroso*-derivative which is decomposed by concentrated sulphuric acid yielding nitrous oxide and isocamphor. This fact seems to confirm the authors' view that isocamphor is a derivative of metacymene (compare this vol., i, 88). W. J. P.

Monoketazocamphadione. By ENRICO RIMINI (*Gazzetta*, 1896, **26**, ii, 290—292).—Monoketazocamphadione,  $C_8H_{14}<\begin{matrix}CO\\|\\CN_2\end{matrix}$, combines with potassium hydrogen sulphite, yielding a *salt* of the composition $C_{10}H_{15}N_2SO_4K,2H_2O$, which is purified by precipitation from its aqueous solution by alcohol; it crystallises in lustrous, yellow scales, which do not decompose at 220°. When boiled with dilute hydrochloric acid, it gives azocamphanone, and when heated with concentrated hydrochloric acid in a current of steam, it yields azocamphanone, which decomposes, yielding camphadione; hydrazine hydrochloride is found in the solution.

The behaviour of monoketazocamphadione is thus similar to that of aliphatic diazo-compounds which combine with alkali hydrogen sulphites giving additive products which yield hydrazine on hydrolysis. W. J. P.

Derivatives of Dihydro-cis-campholytic Acid. By E. B. HARRIS (*Amer. Chem. J.*, 1896, **18**, 692—694).—The results of this investigation have already been described in a paper by Noyes (Abstr., 1896, i, 695). A. G. B.

Camphoric Acid. By WILLIAM A. NOYES (*Amer. Chem. J.*, 1896, **18**, 685—692. Compare Abstr., 1895, i, 187, 295, 552).—Most of the results described have already appeared elsewhere (Abstr., 1896, i, 695).—*Ethylic amidolauronate* is a mobile, strongly basic liquid, with an ammoniacal, aromatic odour; its *sulphate*,

$$(NH_2\cdot C_8H_{14}\cdot COOEt)_2,H_2SO_4,$$

was prepared.

*Dihydro-*cis*-campholytic acid* is prepared by reducing *cis*-campholytic acid with sodium in amylic alcohol; it is an oily liquid, smelling of valeric acid, boiling at 244°, almost insoluble in water, and of sp. gr. = 0·9833 at 20°; it is stable towards a cold solution of potassium permanganate. The *amide*, $C_8H_{15}\cdot CONH_2$, melts at 161°. *Cis*-campholytic acid boils at 255—256°, and *cis-trans*-campholytic acid at 240—243°.

*α-Bromodihydro-*cis*-campholytic acid* was prepared, after Baeyer's prescription (Abstr., 1888, 1075), from the dihydro-acid by treatment with phosphorus pentachloride and bromine. It crystallises from formic acid in needles and melts at 129—130°; when it is treated with cold alcoholic potash, *cis*-campholytic acid is regenerated.

Armstrong's formula for camphor is held to be disproved because *cis*-campholytic acid is not Δ^1-tetrahydroxylylic acid. A. G. B.

Constitution of Isocamphoronic acid. By J. C. W. FERDINAND TIEMANN (*Ber.*, 1896, **29**, 2612—2615).—The author ascribes to isocamphoronic acid the constitution $COOH\cdot CMe_2\cdot CH(CH_2\cdot COOH)_2$, because acetic chloride converts it into an anhydromonocarboxylic acid, which yields terpenylic acid under the influence of concentrated sulphuric acid; isocamphoronic acid also gives rise to terpenylic acid when treated with concentrated sulphuric acid, carbonic oxide being eliminated in each case.

Active α-dihydroxydihydrocampholenic acid, when oxidised, yields optically inactive isoketocamphoric acid, an observation which accords with the formula for the latter substance already suggested,

$$OMe\cdot CMe_2\cdot CH(CH_2\cdot COOH)_2.$$

M. O. F.

The Sap of Antiaris Toxicaria (Upas Tree). By HEINRICH KILIANI (*Arch. Pharm.*, 1896, **234**, 438—451).—Ether extracts *antiarol*, and some of the *resin*; the rest of the resin is removed by successive precipitations with alcohol; by concentrating the alcoholic solution and adding water, *antiarin* is obtained. The sap also contains a considerable amount of potassium nitrate.

Antiarol, $OH\cdot C_6H_2(OMe)_3$, forms white crystals, melting at 146°; it is identical with the 1:3:4:5-hydroxytrimethoxybenzene (Will, *Ber.*, 1888, **21**, 612), and is thus closely related to the iretol of De Laire and Tiemann (Abstr., 1894, i, 48). Its *monobenzoyl* derivative melts at 117°.

Antiar-resin, perhaps $C_{24}H_{36}O$, crystallises in needles, and melts at 173·5°; it is chemically very inert.

Antiarin, $C_{27}H_{42}O_{10} + 4H_2O$, crystallises in rhombic or hexagonal plates, and softens at 220°, melting finally at 225°. It is a poisonous glucoside; indeed, the sap is used for poisoning arrows. When hydrolysed with dilute alcoholic hydrochloric acid, it is converted into antiarigenin and antiarose. *Antiarigenin*, $C_{21}H_{30}O_5$, is a crystalline substance, and melts at about 180°, after first turning deep yellow at 180°. *Antiarose*, $C_6H_{12}O_5$, is isomeric with rhamnose; it was not isolated, but was oxidised with bromine and water to *antiaronic acid*, $C_5H_{11}O_4{\cdot}COOH$, the *lactone* and amorphous *calcium* salt of which were analysed. The lactone crystallises in prisms, and softens at 168°, melting finally at 180°; its specific rotation $[\alpha]_D = -30°$.

C. F. B.

Palm Dragon's-blood. By Karl Dieterich (*Arch. Pharm.*, 1896, **234**, 401--437).—The dragon's-blood examined was a red substance imported in sticks ("*in bacillis*"), which form is less adulterated than the others, and was presumably derived from the fruits of *Daemonorops Draco* (Sumatra); it melted at 70°. If the crude resin is extracted with ether, and alcohol added, *dracoalban* is precipitated. If the ether alcoholic solution is then evaporated to dryness, light petroleum extracts *dracoresen* from the residue, and leaves a mixture of pure resins, of a red colour; this was shown to consist of the *dracoresinotannol* salts of benzoic and benzoylacetic acids. Of the above substances, the crude resin contains in 100 parts: dracoalban 2·5; dracoresen 13·58; red resin (mixture of ethereal salts) 56·86. In addition it contains a resin insoluble in ether, 0·33; a black, amorphous phlobaphene (an oxidation or decomposition product of a tannin; soluble in alkalis) 0·03; plant remains 18·40; ash 8·30.

Dracoalban, $C_{20}H_{40}O_4$, is a white, amorphous powder, becoming strongly electrified when rubbed; it softens at 192—193°, and blackens and decomposes above 200°. It is chemically rather inert, but yields a *trinitro*-derivative, which can be reduced to a *triamido*-derivative, and this yields a (mono ?) *acetyl* derivative; these are all amorphous.

Dracoresen, $C_{26}H_{44}O_2$, is a bright yellow, amorphous resin, melting at 74°; it is chemically very inert. A possible indication was obtained of menthol among its products of hydrolysis.

The red resin consisted mainly of dracoresinotannol benzoate; the benzoylacetate was relatively small in amount. The *dracoresinotannol*, $C_8H_9O{\cdot}OH$, obtained from it on hydrolysis is a bright brown, amorphous powder; it softens at 100—105°, but then decomposes without melting. It yields a *potassium* and a *monacetyl* derivative, both brown and amorphous; nitric acid converts it into picric acid; and on dry distillation it yields benzene, toluene, and probably cinnamene and phenylacetylene, together with phenol, resorcinol, pyrogallol, and acetic acid, and possibly phloroglucinol and creosote. Other products of the hydrolysis of the resin, in addition to dracoresinotannol, are benzoic acid, acetic acid, and acetophenone, the two last coming respectively from the "acid" and "ketone decomposition" of the benzoylacetate. It is pointed out that the benzoylacetate can exist in a tautomeric form as a hydroxycinnamate, which suggests that it may have originated from the oxidation of a cinnamate, for some previous observers have found cinnamic acid in the crude resin.

C. F. B.

Zanzibar Copal. By Stephan (*Arch. Pharm.*, 1896, 234, 3, 552—560).—The crude resin was purified by the precipitation of its alcoholic solution with water. The aqueous solution then contained a yellowish, bitter principle, which could not be obtained crystalline, and was not hydrolysed by dilute sulphuric acid. The resin was then dissolved in alcohol and ether, and extracted with dilute aqueous potash, two isomeric acids being thus removed, whilst an ethereal oil and two resins were left behind in the ethereal solution.

Trachylolic acid, $OH{\cdot}C_{54}H_{85}O_3(COOH)_2$, melts at 165°, but can be obtained in sphæro-crystals melting at 168°. It is only slightly soluble in acetone, ether, and chloroform, and is precipitated in alcoholic solution by lead acetate. It yields a *monacetyl* derivative which is only slightly soluble in carbon bisulphide, and a *monobenzoyl* derivative. The analysis of its potassium and copper salts shows that it is probably dibasic. The isomeric *isotrachylolic acid* is also a dibasic hydroxy-acid. It melts at 105—107°, is readily soluble in acetone, &c., and in alcoholic solution is not precipitated by lead acetate. The *acetyl* derivative is soluble in carbon bisulphide.

a-Copal-resen, $C_{41}H_{68}O_4$, melts at 75—77°, is insoluble in potash, soluble in ether, and does not yield an acetyl derivative. Its alcoholic solution has a rotation of $\alpha = +\ 12{\cdot}56°$. *β-Copal-resen* is insoluble in ether, and decomposes at 140° without melting, The resin contains 80 per cent. of trachylolic acid, 4 per cent. of the isomeride, and 6 per cent. of the resens. A. H.

Resin of Gutta Percha. By GABRIELE TASSINARI (*Gazzetta*, 1896, **26**, ii, 248—256).—The resin of gutta percha, after extracting the gummy matter by alcohol, dissolves in concentrated soda, and on distilling the solution at 160—180°, a liquid (1) passes over. The residue when extracted with water gives a red liquid in which a flocculent precipitate (2) is suspended; on acidifying the mother liquor with hydrochloric acid, a dark-coloured resin (3) sinks, whilst a flocculent precipitate (4) forms in the liquid. The mother liquor, on distillation under reduced pressure, gives an acid distillate (5) and a residue (6) which on extraction with alcohol becomes colourless; after distilling off the alcohol from the extract, a liquid residue is obtained, consisting of an upper layer (7) of fruity odour, and a lower one (8).

The liquid (1) consists of two layers of which the lower is a dilute aqueous solution of methylic alcohol, whilst the upper contains a *limonene*, $C_{10}H_{16}$, and an aldehyde, $C_{10}H_{16}O$, probably geranaldehyde. The limonene does not give a solid bromide or hydrochloride, and when treated with amylic nitrite and hydrogen chloride yields a crystalline *substance* melting and decomposing at 84°. The soft dark product (2) after being freed from a black oil by treatment with benzene, yields a white, crystalline, neutral *substance*, $C_{10}H_{20}O_2$, which melts and decomposes at 270°. The product (3) is a dark, soft resin, soluble in alcohol, ether, benzene, acetic acid and alkali carbonates, and constitutes about two-thirds of the original resin; it carbonises on heating, and when treated with zinc dust gives a black oil which seems to contain homologues of benzene.

The fraction (4) when crystallised from benzene yields, when purified, a "*xyletinic acid*," $C_9H_{10}O_3$, in lustrous, colourless crystals, melting at 156—157°. Acetic acid was separated from the product

(5), and fraction (6) contains isouvitic acid. The liquid (7) yields isouvitic acid and probably geranaldehyde; the latter gives isogeranic acid on oxidation. W. J. P.

Raphanol, a substance contained in the root of Raphanus niger, and other Cruciferæ. By HENRI MOREIGNE (*J. Pharm.*, 1896 [6], 4, 10—16).—From the distillate obtained from the aqueous extract of the root of *Raphanus niger* the author isolated a crystalline substance, *raphanol*, $C_{29}H_{58}O_4$, which melts at 62°, decomposes about 300°, and is soluble in ether, chloroform, benzene, and light petroleum. It appears to be the lactone of an acid, but contains hydroxyl groups as it yields an *acetyl* derivative, melting at 122—123°. Lack of material prevented the author from carrying the investigation further. M. W. T.

A Glucoside contained in Adonis æstivalis, L. By NICOLAI KROMER (*Arch. Pharm.*, 1896, **234**, 452—458).—After the plant had been extracted with 96 per cent. alcohol at 60°, the alcoholic extract was evaporated down under diminished pressure, and extracted successively with light petroleum, ether, and chloroform. Chloroform extracted a new glucoside, $C_{25}H_{40}O_{10}$; this is a yellow, amorphous substance, very soluble in water and bitter to the taste; it is contained in the plant to the extent of 0·22 per cent. Its physiological action resembles that of the adonidin of *Adonis vernalis*, but is very much weaker. C. F. B.

Quercetin and its Derivatives. By JOSEF HERZIG (*Monatsh.*, 1896, 421—428. Compare Abstr., 1895, i, 387, 554, &c.).—The melting point of tetracetylluteolin is 223—226°, and not, as is stated by A. G. Perkin (Trans., 1896, 210), 213—215°. The author prepares triethylluteolin from its acetyl derivative, which is readily hydrolysed and has a molecular weight of 408, that calculated from the formula $C_{15}H_6O_6Et_3Ac$ being 412. Triethylluteolin (luteolin triethyl ether) is yellow, as Perkin has stated (*ibid.*, 800); it melts, however, at 140—143°, and not at 131—132°. The substance obtained from the crude extract does not appear to be the same as that prepared by the direct ethylation and acetylation of luteolin.

When diethyleuxanthone is warmed with concentrated sulphuric acid, complete decomposition ensues, and *fisetinsulphonic acid*,

$$C_{15}H_9O_6{\cdot}SO_3H,$$

is formed. This may be obtained directly from fisetin, but is most readily prepared by heating the alkylfisetins with about 10 times their weight of sulphuric acid during 4—5 hours on the water bath; it crystallises in beautiful, yellow needles, does not melt at 300°, dissolves readily in alcohol and water, but is insoluble in ether; its aqueous solution gives a green coloration with ferric chloride.

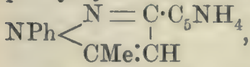
The author states that he is continuing the investigation of morin, and also the work of Ciamician and Silber on the constitution of maclurin. A. L.

Digitoxin. By HEINRICH KILIANI (*Arch. Pharm.*, 1896, **234**, 481—489. Compare Abstr., 1896, i, 59, ii, 552). The substance previously described as β-digitoxin by the author is identical in all respects with Schmiedeberg's digitoxin. The supposed difference between the composition of the two has been found to be due to the difficulty with which digitoxin undergoes complete combustion. When hydrolysed with alcoholic hydrogen chloride, it yields digitoxigenin and digitoxose. The former of these melts at 225—230°, and, like digitoxin, is difficult to burn; it yields a crystalline *potassium salt*, $C_{22}H_{31}O_4K$, and crystalline precipitates with the chlorides of barium and calcium, and the author now proposes for it the formula $C_{22}H_{32}O_4$ instead of $C_{21}H_{32}O_4$. Digitoxose crystallises in prisms or tablets, melts at 101°, and has a rotation $[\alpha]_D = +46°$; its empirical formula is $C_3H_6O_2$, as previously found, and its molecular formula is probably $C_9H_{18}O_6$, although this requires experimental confirmation. It follows from this that the formula for digitoxin is $C_{31}H_{50}O_{10}$. Experiments carried out with the seeds of Digitalis show that digitoxin does not itself occur in these. A. H.

Pyridine Alkyl Hydroxides. By ALBERT B. PRESCOTT and S. H. BAER (*J. Amer. Chem. Soc.*, 1896, **18**, 247—251).—Pyridine propiodide (Abstr., 1896, i, 316), on treatment with moist silver oxide, yields a solution of *pyridine propohydroxide*, which precipitates salts of lead, silver, copper, iron, aluminium, chromium, cobalt, and nickel, an excess of the hydroxide solution redissolves the precipitates obtained with lead and aluminium. The solution also gives an alkaline reaction with litmus, phenolphthaleïn, brazil-wood, cochineal, hematoxylin or methyl-orange. Pyridine itself does not give an alkaline reaction with phenolphthaleïn or hematoxylin. The solution acquires a red colour when heated, and on evaporation yields a black residue, which is soluble in water. *Pyridineisopropohydroxide* has also been prepared. It resembles the normal compound in all the above-mentioned details. The *carbonate, sulphate* and *platinochloride* were obtained in a crystalline form. J. J. S.

α-Acetoacetylpyridyl [2-Acetoacetylpyridine]. By KARL MICKO. (*Montash.*, 1896, **17**, 442—461).—Ethylic picolinate and acetone condense when treated in the manner described by Weidel (compare this vol., i, 104). The product, *α-acetoacetylpyridine*, $C_5NH_4\cdot CO\cdot CH_2\cdot COMe$, crystallises in monoclinic needles or transparent prisms; $a:b:c = 0{\cdot}4679:1:0{\cdot}4824$, $\beta = 82°2'$. It melts at 49—50°, is volatile at elevated temperatures, slight sublimation occurring at the ordinary temperature, and dissolves readily in alcohol, ether, chloroform, benzene and boiling light petroleum but is insoluble in water. Its alcoholic solution, when mixed with ferric chloride, gives the red coloration characteristic of β-diketones. The *hydrochloride* crystallises in clear hygroscopic crystals and decomposes, evolving irritating vapours at 100°. The *platinochloride*, $(C_9H_9NO_2)_2,H_2PtCl_6 + 2H_2O$, forms yellowish-red tables and is exceedingly unstable. The diketone yields two *compounds* with mercuric chloride; the first is obtained when a strongly acid alcoholic solution of the base is mixed with an alcoholic solution of mercuric chloride, and forms small, shining pyramidal crystals of the composition $C_9H_9NO_2,HCl,HgCl_2 + 2H_2O$, the second substance is produced on warming the foregoing compound with 60—70 per cent. alcohol, and forms silky, colourless needles which have the formula $C_9H_9NO_2,HgCl_2$.

a-Acetoacetylpyridine is decomposed into acetone and picolinic acid when heated with concentrated potash or soda. When warmed with phenylhydrazine acetate, it yields 3-*pyridyl*-1-*phenyl*-5-*methylpyrazole*,



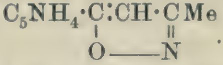
$$\mathrm{NPh}<\begin{array}{l}\mathrm{N = C\cdot C_5NH_4}\\ \qquad\ |\\ \mathrm{CMe\colon CH}\end{array}$$

which forms a yellowish, thick oil, distils at 215° under 15 mm. pressure, and does not solidify at $-20°$; it is insoluble in water and light petroleum, but dissolves readily in alcohol and ether. The *ethiodide*, $C_{15}H_{13}N,EtI$, forms lemon-yellow aggregates of leaves, and melts and decomposes at 181—183°; on shaking with silver chloride, the corresponding *chloro*-compound is obtained in the form of deliquescent needles; it yields a *platinochloride*,

$$(C_{15}H_{13}N_3)_2,Et_2PtCl_6,$$

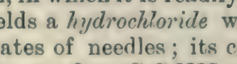
which crystallises in dark orange-red grains.

Two compounds are obtained on treating *a*-acetoacetylpyridine with hydroxylamine, namely, a *monoxime*, $C_9H_{10}N_2O_2$, and a *dioxime*, $C_9H_{11}N_3O_2$, the monoxime is produced when the calculated quantity of sodium hydroxide is used, and forms crystals melting at 78° (uncorr.); it dissolves readily in alcohol, ether and hot chloroform. When treated with acetic acid saturated with hydrogen chloride, it suffers isomeric change, being converted into a *substance* which crystallises from boiling light petroleum in prisms melting at 48° (uncorr.); the new compound forms a deliquescent *hydrochloride*, is insoluble in water but dissolves readily in alcohol, and is doubtless an isoxazole derivative of the constitution



$$\begin{array}{l}\mathrm{C_5NH_4\cdot C\colon CH\cdot CMe}\\ \qquad\quad |\qquad\ \ \|\\ \qquad\ \ \mathrm{O}\!-\!\!-\!\!-\!\mathrm{N}\end{array}$$

. The *dioxime* is produced when the monoxime is treated with excess of hydroxylamine in presence of free hydrochloric acid; it crystallises from hot water in small, four-sided prisms melting at 146—147° and decomposing at about 150° with evolution of gas; when treated with acetic acid and hydrogen chloride, it yields an *isoxazole* derivative isomeric with that obtained from the monoxime by a similar process. This substance crystallises from cold, light petroleum, in which it is readily soluble, in shining prisms melting at 37·5°; it yields a *hydrochloride* which separates from water in the form of aggregates of needles; its constitution is possibly represented by the formula



$$\mathrm{N}<\begin{array}{l}\mathrm{O\!-\!\!-\!C\cdot C_5NH_4}\\ \qquad\ \ \|\\ \mathrm{CMe\cdot CH}\end{array}.$$

Ammonia acts on the diketone with production of, in the first instance, an *ammonium* compound, $C_5NH_4\cdot CO\cdot CH(NH_4)\cdot COMe$, which separates from the alcoholic solution as a fine crystalline precipitate, but decomposes when heated at 110—120° with production of the *amido*-derivative, $C_5NH_4\cdot CO\cdot CH\colon CMe\cdot NH_2$. The latter separates from alcohol in monoclinic tables; $a : b : c = 0·7004 : 1 : 0·9785$; $\beta =$ 71 54′. It dissolves readily in alcohol and boiling water, but is insoluble in benzene and petroleum, and melts at 149—150°; it reacts with phenylhydrazine and hydroxylamine, and is decomposed at the ordinary temperature by dilute hydrochloric acid with production of ammonium chloride and α-acetoacetylpyridine hydrochloride.

The diketone is reduced by zinc dust and acetic acid, a *substance* $C_9H_{11}NO_2$, crystallising in colourless needles, being formed. This melts at 74°, is readily soluble in water, alcohol, ether and ethylic acetate, but is insoluble in light petroleum; it yields a *platinochloride*,

$$(C_9H_{11}NO_2)_2,H_2PtCl_6,$$

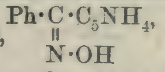
in beautiful, orange-red crystals; when treated with hydroxylamine, it forms an *oxime*, $C_9H_{12}N_2O_2$, melting at 120°, and crystallising in small prisms readily soluble in alcohol and ether but insoluble in light petroleum; on oxidation with potassium permanganate, it yields picolinic and acetic acids, but, on treatment with alkali, it yields neither picolinic acid nor acetone as does the original diketone. These facts are all in accordance with the supposition that the reduction product is a ketonic alcohol having the formula $C_5NH_4 \cdot CH(OH) \cdot CH_2 \cdot COMe$.

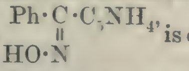
A. L.

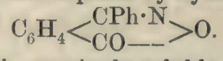
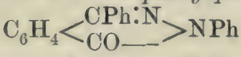
β-Benzoylpicolinic Acid and β-Pyridyl Phenyl Ketone. By Berthold Jeiteles (*Monatsh.*, 1896, 17, 515—527).—The author describes in detail the preparation of β-benzoylpicolinic acid (compare Abstr., 1887, 737). The *hydrogen silver* salt,

$$COPh \cdot C_5NH_3 \cdot COOAg,COPh \cdot C_5NH_3 \cdot COOH,$$

crystallises in thick prisms, and is not affected by light.

Anti-*β-pyridylphenylketoxime*,  $\underset{N \cdot OH}{\overset{\Vert}{Ph \cdot C \cdot C_5NH_4}}$, is prepared by the action of hydroxylamine on the crude product obtained by heating β-benzoylpicolinic acid at 147—150°; it is insoluble in water, but dissolves readily in hot alcohol, and forms aggregates of crystalline granules; it sinters at 136°, and melts at 141—143°. When dissolved in ether and digested during 30 hours with phosphorus pentachloride, it yields a product melting at 59—60°, which, on hydrolysis, yielded benzoic acid and an oil; the latter commenced to distil at the boiling point of β-amidopyridine, but consisted, for the most part, of β-pyridyl phenyl ketone produced by the hydrolytic action of the hydrogen chloride on the oxime. The production of benzoic acid supplies the necessary proof of the configuration of the oxime.

Syn-*β-pyridylphenylketoxime*,  $\underset{HO \cdot N}{\overset{\Vert}{Ph \cdot C \cdot C_5NH_4}}$, is obtained when 2½ molecular proportions of hydroxylamine are employed; this also is insoluble in water and readily soluble in hot alcohol, but it crystallises in stout prisms melting at 162—163°. When dissolved in dilute hydrochloric acid and reprecipitated by sodium carbonate, it undergoes a partial transformation into the anti-oxime, and the resulting mixture melts at 140—153°. When treated in ethereal solution with phosphorus pentachloride, a yellowish crust is slowly deposited, from which the ethereal solution is decanted, shaken with water and then with soda, the resulting precipitate being added to the above insoluble crust, and hydrolysed by means of strong hydrochloric acid. Aniline and β-pyridyl phenyl ketone were discovered in the product, no benzoic acid being detectable ; the alkaline solution was found to contain nicotinic acid. The formation of aniline and nicotinic acid serves to characterise the oxime as a syn-derivative.

When β-benzoylpicolinic acid is treated with hydroxylamine hydrochloride and soda, a *sodium* salt, $NOH{:}CPh\cdot C_5NH_3\cdot COONa$, is obtained in the form of large, shining prisms ; it is decomposed by hydrochloric acid, yielding *phenylpyridoorthoxazinone*,  $C_6H_4{<}\begin{matrix}CPh\cdot N\\ CO\text{---}\end{matrix}{>}O$. The latter crystallises from alcohol, in which it is sparingly soluble, in the form of shining scales melting at 187—193° ; the *hydrochloride* crystallises with difficulty. Phenylhydrazine acts on β-benzoylpicolinic acid with formation of 1:3-*diphenylquinolineazone* (or 1:3-*diphenylpyridopyradazone*),  $C_6H_4{<}\begin{matrix}CPh{:}N\\ CO\text{---}\end{matrix}{>}NPh$; it crystallises in yellowish, shining tablets, dissolves somewhat sparingly in boiling alcohol, is insoluble in sodium carbonate solution, and melts at 233—235°. The *hydrochloride* crystallises in thin, yellow tables, and the *nitrate* in radiate groups of flat leaflets.
A. L.

Cincholeuponic Acid. By ZDENKO H. SKRAUP (*Monatsh.*, 1896, 17, 365—394).—When the hydrochloride of cincholeuponic acid is heated with about ten times its weight of strong sulphuric acid at 260—270° during 2 hours, it yields 4-methylpyridine (γ-picoline) and two methylpiperidinecarboxylic acids which were isolated, in the forms of a crystalline platinochloride and an aurochloride respectively. The *platinochloride*, $(C_7H_{13}NO_2)_2,H_2Pt_2Cl_6$, forms orange-yellow crystals which melt and intumesce at 200—202°, and dissolves with difficulty in water but is readily soluble in alcohol ; the *aurochloride*,

$$C_7H_{13}NO_2,HAuCl_4,$$

crystallises in microscopic leaflets, dissolves readily in water and melts at 174° ; these salts are derived from different acids, as the latter yields a crystalline compound when decomposed with hydrogen sulphide, whilst the former gives an amorphous substance, which, on treatment with gold chloride, forms an *aurochloride* not identical with the foregoing, and crystallising in small plates melting at 197—198°.

Cincholeuponic acid, when treated with acetic chloride, yields *acetylcincholeuponic anhydride*, $C_8H_{10}NO_3Ac$, which crystallises from a mixture of alcohol and ether in large prisms melting indefinitely at 130—131°, and is readily hydrolysed by warm water with production of *acetylcincholeuponic acid*, $C_8H_{12}NO_4Ac$. The latter forms a crystalline mass, and melts at 168° ; its aqueous solution, on admixture with copper acetate, yields an intensely green *copper* salt, $C_8H_{10}AcNO_4Cu + 2H_2O$, which crystallises in microscopic aggregates.

Phosphorus pentachloride reacts with the hydrochloride of cincholeuponic acid, and the product when poured into water gives a yellow oil. The latter, on analysis, gave numbers in agreement with the formula $C_{27}H_{30}P_5Cl_{11}N_3$, but could not be purified ; it is not affected by boiling baryta-water but dissolves in boiling nitric and hydrochloric acids.

Concentrated chromic acid mixture attacks cincholeuponic acid liberating carbonic anhydride and hydrogen cyanide. Potassium permanganate also effects a partial oxidation, and the product contains *leuponic acid*, $C_7H_{11}NO_4$; the latter also occurs in the mother liquors of the crude hydrochloride of cincholeuponic acid, and is separated in the following manner. The hydrochloric acid is precipitated by the correct amount of silver oxide, and the filtrate evaporated; the crystals which separate in a few days are filtered off, and the mother liquors are twice subjected to similar treatment. In this way a quantity of a sparingly soluble powder is obtained which crystallises from hot water in irregular prisms, and melts and decomposes at 259—260°; it has the above composition, and acts as a dibasic acid. It forms a *hydrochloride*, $C_7H_{11}NO_4,HCl$, which crystallises in thick, facetted prisms, dissolves readily in water but is very sparingly soluble in strong hydrochloric acid, and melts indefinitely at 216—220°; it yields a crystalline *platinochloride* and an *aurochloride*, $C_7H_{11}NO_4,HAuCl_4 + H_2O$; the latter is sparingly soluble in cold water, and melts at 201—202°. *Potassium leuponate* crystallises in masses of microscopic leaflets.

Acetylleuponic anhydride, $C_7H_8NO_3Ac$, is prepared by the action of a large excess of acetic anhydride on leuponic acid; it dissolves readily in acetic acid, sparingly in alcohol, and forms crystalline aggregates melting indefinitely at 161°; it dissolves in warm water yielding *acetylleuponic acid*, $C_7H_{10}NO_4Ac$, which is more sparingly soluble in water than the anhydride, and melts at 204°. When hydrogen chloride is passed through an alcoholic solution of leuponic acid, crystals of the hydrochloride are at first deposited but gradually redissolve, and a product is obtained which does not crystallise but, on admixture with platinum tetrachloride, yields a sparingly soluble, anhydrous *platinochloride* $C_7H_9NO_4Et_2,H_2PtCl_6$; the production of this substance serves to prove that leuponic acid, like cincholeuponic acid, contains two carboxyl groups.

When cincholeuponic acid is heated with lime in an iron tube, and the distillate is neutralised with hydrochloric acid, extracted with ether and evaporated, the residue being extracted with alcohol, the soluble portion yields a *platinochloride*, $C_7H_{15}N,H_2PtCl_6$, which crystallises in orange-yellow, irregular prisms, melts and decomposes at 194—196°, and dissolves readily in water; its properties suggest that this compound is an acid salt of chloroplatinic acid, whilst such compounds are not formed by pyridine, piperidine or pyrollidine bases. The above ethereal extract on fractional distillation yields a liquid boiling at 150—200°; it gives the pyrroline reaction with a pine-shaving and has the chloroform-like odour of pure pyrroline; on analysis it gives numbers in agreement with a tetramethylpyrroline. It is probable, however, that such compounds are formed by a complicated series of reactions, and do not indicate that cincholeuponic acid is a derivative of pyrroline.

Ethylic cincholeuponate yields a *platinochloride*,

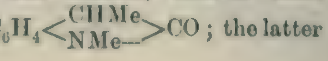
$$C_8H_{11}NO_4Et_2,H_2PtCl_6,$$

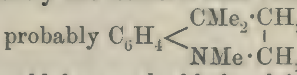
the author's original statement to the contrary having been due to the employment of unfavourable conditions; the substance crystallises in beautiful, anhydrous leaflets, and melts at 181°. Methylic iodide acts on the ethylic salt in presence of potassium carbonate, giving *diethylic methylcincholeuponate methiodide*, $C_8H_{10}MeNO_4Et_2,MeI$, which dissolves readily in methylic alcohol, sparingly in chloroform and in 4 parts of cold water; it forms colourless crystals, melts at 176°, and sublimes if strongly heated, but the distillate is no longer crystalline; it is optically active, a ½ per cent. solution in water at 20° in a 100 mm. tube producing a rotation $\alpha = -0{\cdot}2155°$; by its interaction with silver chloride, a syrup is obtained which yields a crystalline *platinochloride* and *aurochloride*, of which the former crystallises in minute leaflets melting at 210—213°, whilst the latter separates from hot water in large, golden, irregular leaflets and melts at 80—82°. If the methiodide is heated with silver hydroxide, it undergoes partial hydrolysis, and the resulting syrup yields an *aurochloride*, $C_8H_{11}Me_2NO_4,EtAuCl_4$, which is very unstable and forms rectangular tables melting at 90—95°; the corresponding *platinochloride* melts at 197—198°. The behaviour of the foregoing compounds is similar to that of tropinic acid derivatives; the latter, however, differ in some respects, as they are decomposed by a warm solution of potassium carbonate, whilst the methiodide in question is not affected; in presence of alcohol, however, or when potassium carbonate is added to the boiling aqueous solution, hydrolysis does occur, and an isomeric *methiodide*, $C_8H_{10}MeNO_4Et_2,MeI$, rapidly separates. The new substance crystallises from water in stout prisms melting at 120°, and dissolves in less than its own weight of water; examined in a polarimeter under the above conditions its rotation is $\alpha = -0{\cdot}4450°$; it is acted on by silver chloride, and the product yields a resinous *aurochloride* and a *platinochloride* crystallising in anhydrous microscopic grains which melt and decompose at 216°. When heated above its melting point, the new methiodide sets to a resin which contains a substance crystallising from water in tables and melting at 134°.

Both of the foregoing methiodides are decomposed by caustic potash, and the latter must be added to the amount required for complete hydrolysis and liberation of iodine, in order to render the solutions permanently alkaline; the product, in both cases, contains diethylic dimethydihydroxycincholeuponate. A. L.

Indolinones. By KARL BRUNNER (*Monatsh.*, 1896, **17**, 479—496. Compare Abstr., 1896, i, 169 and 625).—Five grams of isobutyrylphenylhydrazide is heated with six times its weight of lime at 230—260° during 4 hours; the mass is then mixed with excess of hydrochloric acid, boiled in order to decompose unaltered hydrazide, and distilled with steam; the distillate is extracted with ether, and the ethereal extracts shaken with soda, dried and evaporated. The residue, which consists of indolinone, gradually sets to a mass of crystals, and may be crystallised from petroleum; it melts at 47° and has all the properties of the substance obtained by the author on oxidising 1′:3′:3′-trimethylindolium hydroxide (*loc. cit.*).

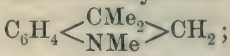
Acetophenylmethylhydrazide, when treated in a similar manner, gives a small quantity of the corresponding indolinone, namely, methyloxindole.

Propionylphenylmethylhydrazide, in like fashion, affords some quantity of 1′:3′-*dimethyl-2′-indolinone*,  $C_6H_4{<}\substack{CHMe\\NMe}{>}CO$; the latter forms microscopic grains with hexagonal outlines, melts at 22·5—23°, and boils at 273—277° under 742 mm. pressure; it has a faint, blossom-like odour, is soluble in water only with difficulty, but dissolves readily in alcohol, ether, and cold concentrated acids, being reprecipitated, in the latter instance, on the addition of water. It reduces Fehling's solution after continued heating, ammoniacal silver solution suffering reduction even in the cold. The *aurochloride*, $(C_{10}H_{11}NO)_2,HAuCl_4$, is obtained as a dark red oil which solidifies when the containing vessel is scratched. The *mercuric chloride* compound, $C_{10}H_{11}NO,HgCl_2$, is precipitated as colourless leaflets which melt at 118°. On bromination, the indolinone yields a *tribromo*-derivative, $C_{10}H_8NBr_3O$, which crystallises in aggregates of yellow needles, and melts at 160°; it is not dissolved by strong aqueous potash, but is attacked by alcoholic potash, bromine being eliminated. A. L.

Constitution of the Bases formed by the action of Alkyl Iodides on Indoles. By Giacomo L. Ciamician (*Ber.*, 1896, 29, 2460—2465).—In the following abstracts it is shown that the difference between synthetical 2′:4′-dimethyltetrahydroquinoline and the isomeric base obtained by the action of methylic iodide on indole or indoles containing methyl groups in the pyridine ring is more than one of stereoisomerism, for the two substances react differently with mercuric acetate; probably the base from indole has its two methyl groups attached to the 4′ carbon atom. Further, although synthetical trimethyldihydroquinoline and the base from indole isomeric with 1′:2′:4′-trimethyltetrahydroquinoline are oxidised to the same product, yet this synthetical trimethyltetrahydroquinoline itself is not so oxidised; consequently the isomeric base from indole must have a different constitution, probably  $C_6H_4{<}\begin{matrix}CMe_2\cdot CH_2\\ | \\ NMe\cdot CH_2\end{matrix}$, in which case the trimethyldihydro-base would have a double bond in the 2′-3′ position. This view of their constitution is in harmony with the fact that two methyl groups can be introduced into the trimethyldihydro-base, and into an homologous dimethylethyldihydro-base. C. F. B.

Trimethyldihydroquinoline. By Giacomo L. Ciamician and Antonio Piccinini (*Ber.*, 1896, 29, 2465—2471. Compare preceding abstract).—Synthetical 2′:4′-dimethyltetrahydroquinoline is oxidised to 2′:4′-dimethylquinoline by heating it for 6 hours at 150° with a 50 per cent. aqueous solution of mercuric acetate; the isomeric base from indole is not so oxidised.

Trimethyldihydroquinoline, when oxidised with alkaline permanganate or a chromic acid mixture, yields Brunner's trimethylindolinone (Abstr., 1896, i, 625), and so does the base from indole isomeric with the substance next described. 1′:2′:4′-*Trimethyltetrahydroquinoline* itself is not so oxidised, however; it was prepared by digesting 2′:4′-dimethyltetrahydroquinoline with methylic iodide at 100°; it boils at about 250° under 759 mm. pressure, and its yellow *picrate* melts at 126—127°.

Brunner's trimethylindolium hydroxide (*loc. cit.*), which may equally well be formulated as a secondary alcohol, can be reduced by heating it at 150° with hydriodic acid and phosphorus. Some trimethylindole is formed, together with 1′:3′:3′-*trimethylindoline*,  $C_6H_4<\genfrac{}{}{0pt}{}{CMe_2}{NMe}>CH_2$; the latter boils at 224—227°; its *hydriodide* melts at 184—185°, and its deliquescent *hydrochloride* at 175°, whilst its *methiodide* volatilises at 204—205°. When it is heated in an oil-bath at 215—230° with hydriodic acid and ammonium iodide, it yields 3′:3′-*dimethylindoline*, which boils at 224—230° under 758 mm. pressure, and yields a pale yellow *platinochloride* melting and decomposing at about 217°. This secondary base is not affected by heating with mercuric acetate, but distillation of its hydrochloride over zinc dust yields 2′:3′-dimethylindole and (probably) 2′-methylquinoline; in these respects it resembles the base from indole isomeric with 2′:4′-dimethyltetrahydroquinoline.

C. F. B.

Relation of Trimethylindole to Alkyldihydroquinolines. By Giacomo L. Ciamician and G. Boeris (*Ber.*, 1896, **29**, 2472—2475. Compare Abstr., 1895, i, 111, 392, and preceding abstracts).—In addition to the products already obtained by distilling trimethyldihydroquinoline hydriodide, the tertiary ammonium iodide of the base from indole, 1′:4′:4′-trimethyltetrahydroquinoline, has now been isolated; the yellow *platinochloride* of this base melts and decomposes at about 208°.

When trimethylindole is treated at 110° with methylic iodide and methylic alcohol, it yields a colourless base, $C_{13}NH_{17}$, which reddens in the air and boils at 128—130° under 21 mm. pressure; its *hydriodide* melts and decomposes at 229°, and yields an indole derivative when distilled; the base itself is homologous with ordinary trimethyldihydroquinoline.

C. F. B.

Action of Ethylic Iodide on 2′-Methylindole. By Giacomo L. Ciamician and Giuseppe Plancher, and in part G. Boeris (*Ber.*, 1896, **29**, 2475—2482. Compare E. Fischer and Steche, Abstr., 1888, 298).—When 2′-methylindole is heated with ethylic iodide and ethylic alcohol for 15 hours at 95—98°, the product contains two bases, the one being the ethyl derivative of the other. These bases were separated from indoles simultaneously formed by dissolving them out with hydrochloric acid; they were converted into acetyl derivatives by boiling with acetic anhydride and sodium acetate, the acetates were separated by fractionation under diminished pressure, and were then decomposed by hydrolysis, in the one case with 20 per cent. alcoholic potash, in the other (that of the ethyl derivative) by boiling with 10 per cent. hydrochloric acid.

The first base, $C_{13}H_{17}N$, is a secondary base already obtained by Fischer and Steche. It boils at 139—140° under 25 mm. pressure, and its yellow *picrate* melts at 189—190°; the *acetyl* derivative is liquid; its *benzoyl* derivative melts at 74—75°, and its compounds with *methylic* and *ethylic iodides* at 189° and 145—146° respectively. The last two are the hydriodides of tertiary bases; the ethyl compound is identical with the hydriodide of the second base obtained by the direct ethylation of 2′-methylindole; the methyl-compound crystallises in rhombic tetrahedra; $a : b : c = 0·9930 : 1 : 0·9089$. The base itself, in boiling alcoholic solution, is reduced by sodium to a base $C_{13}H_{19}N$; the *hydrochloride* of this base melts at 217° and crystallises in monoclinic plates; $a : b : c = 1·3314 : 1 : 1·2841$; $\beta = 86°55'$. The *picrate* melts at 138° and crystallises in the triclinic system ($a : b : c = 1·9727 : 1 : 1·4134$; $\alpha = 113° 36'$; $\beta = 111° 30'$; $\gamma = 63° 18'$); and the *phenylcarbamide* melts at 149—150°; methylic iodide converts it successively into the compounds $C_{13}H_{18}NMe,HI$ and $C_{13}H_{18}NMe, MeI$, which both melt at 192°, the latter decomposing at the same time.

The second base, $C_{13}H_{16}NEt$, is a colourless oil which boils at 138—140° under 18 mm. pressure, and turns red on exposure to the air; the *hydriodide* is identical with the compound of ethylic iodide with the base $C_{13}H_{17}N$; the *acetyl* derivative crystallises in triclinic prisms or tablets ($a : b : c = 1·4653 : 1 : 1·6070$; $\alpha = 84° 49'$; $\beta = 100° 4'$; $\gamma = 86° 4'$), melts at 116—117°, and yields a yellow *platinochloride* which melts at about 200°; the *benzoyl* derivative melts at 125—126°; reduction with sodium in alcoholic solution converts the base itsel into an oily base, $C_{13}H_{18}NEt$, the yellow *picrate* of which melts at 117—119°.

C. F. B.

Action of Sulphur Haloids on Aromatic Amines. By ALBERT EDINGER (*Ber.*, 1896, **29**, 2456—2460. Compare Abstr., 1895, i, 300). —When quinoline is heated with sulphur dichloride, SCl_2, in a sealed tube at 160°, and the product boiled with dilute hydrochloric acid, a *trichloroquinoline*, devoid of basic properties, remains undissolved; it melts at 185—186°.

When the acid solution is nearly neutralised, *3′-chloroquinoline* separates; this is an oil boiling at 255° under 743 mm. pressure; the *hydrochloride* sublimes undecomposed, but melts with intumescence at 210°; the *platinochloride*, with $2H_2O$, melts above 300°; the *sulphate* at 250°, and the reddish-yellow *dichromate* at 119°; the *methiodide* sublimes at 276°. The base itself is oxidised by nitric acid to a chloropyridinemonocarboxylic acid.

When excess of alkali is added to the solution from which the chloroquinoline has been separated, a crystalline substance, *thioquinanthrene*, C_9NH_5S, is obtained; this melts with partial sublimation at 306°, and sublimes at 170° under 28 mm. pressure. It is a feebly basic substance, yielding a yellow *sulphate* which crystallises with $2H_2O$, and a dark-red *methiodide*, also with $2H_2O$, that melts above 360°; when heated with nitric acid in a sealed tube, it appears to yield a mixture of nicotinic acid with a little of a pyridinedicarboxylic acid, and hence, probably, contains the sulphur in the benzene ring. The yields of the three substances are respectively 10, 20, and 40 per cent. The sulphur base is also formed, to the extent of 30—35 per cent., when quinoline is heated with sulphur chloride, S_2Cl_2.

When sulphur bromide, S_2Br_2, is slowly added to quinoline, a reaction occurs; no sulphur base is formed, but a little *tribromoquinoline*, melting at 166°, is obtained, together with the 3′-bromoquinoline of Claus and Collischonn, which is more conveniently prepared by the present method.

C. F. B.

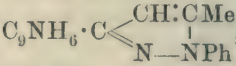
γ-Acetoacetylquinolyl. [4′-Acetoacetylquinoline]. By Hugo Weidel (*Monatsh.*, 1896, 17, 401—420).—*4′-Acetoacetylquinoline*, $C_9NH_6\cdot CO\cdot CH_2,COMe$, is obtained when ethylic cinchonate and acetone are dissolved in anhydrous benzene and treated with sodium ethoxide, the action being completed by warming at 50—60° for a few hours. It forms slender, silky needles, melts at 64—65°, boils at 205—207° (17 mm. pressure), dissolves sparingly in water, but is readily soluble in alcohol, ether, benzene, and in dilute acids or alkalis. Its solution in dilute potash gives an intense blood-red coloration with excess of ferric chloride. The *hydrochloride*,

$$C_{13}H_{11}NO_2,HCl,$$

forms fine, silky, sulphur-yellow needles, and melts at 180—181° (uncorr.); the *oxalate*, $C_{13}H_{11}NO_2,C_2H_2O_4$, crystallises in pale yellow needles, melting at 166—167°; the *platinochloride*,

$$(C_{13}H_{11}NO_6)_2,H_2PtCl_4,$$

forms small, orange-yellow needles, and melts at 192—193°. The *methiodide*, $C_{13}H_{11}NO_2,MeI, + H_2O$, forms large, lustrous, reddish-yellow ortho-rhombic needles, showing pinacoïd faces, and melts at 189—191°. The substance yields compounds with metals, that with *sodium*, $C_{10}H_{10}NaNO_2$, forming small, yellow needles. The latter substance' or even a solution of acetoacetylquinoline in strong potash, decomposes when heated with alkalis with production of acetone and cinchoninic acid.

3-*Quinolyl*-1-*phenyl*-5-*methylpyrazole*,  $C_9NH_6\cdot C{<}\begin{array}{l}CH{:}CMe\\ \quad\;\;\mid\\ N—NPh\end{array}$, is formed when the hydrochlorides of phenylhydrazine and 4′-acetoacetylquinoline are dissolved in water and mixed with sodium acetate; it is practically insoluble in water, but dissolves readily in alcohol, ether, benzene, and light petroleum, and melts at 120°. The crystals are monoclinic, possibly hemihedral; $a:b:c = 0{\cdot}6171:1:0{\cdot}5319$; $\beta = 85°\ 28'$. Hydroxylamine does not yield an isoxazole with γ-acetoacetylquinoline as it does with most β-diketones, but produces the *monoxime*, $C_{13}H_{12}N_2O_2$; this crystallises in lustrous, colourless, triclinic pyramids ($a:b:c = 1{\cdot}1295:1:0{\cdot}9113$; $\alpha = 90°\ 50'$, $\beta = 78°\ 16'$, $\gamma = 88°\ 49'$), melts at 170–171°, is nearly insoluble in water, ether, and benzene, but dissolves readily in hot alcohol, and is rapidly attacked by ammonia and amines.

Amidoacetoacetylquinoline, $C_9NH_6\cdot CO\cdot CH{:}CMe\cdot NH_2$, formed by the action of anhydrous ammonia on the diketone, forms yellowish, monoclinic (?) crystals, melting at 184° (uncorr.), may be heated considerably without undergoing decomposition, and forms salts with various acids. *Anilidoacetoacetylquinoline*, $C_9NH_6\cdot CO\cdot CH{:}CMe\cdot NHPh$, crystallises from benzene in shining, lemon-yellow needles melting at 129·5°, dissolves readily in alcohol and benzene, and sparingly in petroleum and ether; when warmed with dilute hydrochloric acid, it is partially decomposed into its components, but the *hydrochloride*,

$$C_{19}H_{16}N_2O,2HCl,$$

may sometimes be obtained; it forms slender, red needles, and is incompletely dissolved by water owing to partial dissociation.

When γ-acetoacetylquinoline and orthoamidobenzaldehyde are warmed with the calculated quantity of alcoholic soda, 1 molecule of the former condenses with 2 of the latter with production of a new compound for which the author proposes the name *a-diquinolylquinoline*, $C_9NH_5(C_9NH_6)_2$ (compare Friedländer and Eliasberg, Abstr., 1892, i, 1107). It forms long, asbestos-like needles, dissolves readily in benzene, acetic acid, and alcohol, and melts at 150—151° (uncorr.), and is volatile at higher temperatures; the *hydrochloride*, $C_{27}H_{17}N_3,3HCl$, crystallises in dull, yellowish needles, and is partially decomposed by water and by a temperature of 100°. The *platinochloride*,

$$2(C_{27}H_{17}N_3),3H_2PtCl_4,$$

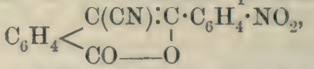
crystallises in bright-yellow, monoclinic needles, and decomposes, without melting, above 200°. The *aurochloride*, $C_{27}H_{17}N_3,3HAuCl_4$, forms beautiful, glistening needles, melts with effervescence at 255°, and is decomposed by water or dilute hydrochloric acid. The *methiodide*, $C_{27}H_{17}N_3,3MeI + 2H_2O$, forms dark-red needles, and melts at 201° (uncorr.). The mother liquors from the α-diquinolylquinolin smell strongly of quinoline and, on distillation with steam, yield an oil boiling at 242°, and having all the properties of quinaldine, $C_{10}H_9N$; the production of the latter is doubtless due to the initial decomposition of the acetoacetylquinoline employed into cinchoninic acid and acetone.

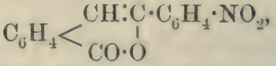
A. L.

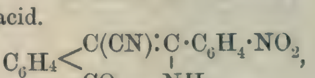
Hexahydroquinolinic Acids. By Emil Besthorn (*Ber.*, 1896, **29**, 2662—2666. Compare Abstr., 1896, i, 252).—The author has described (*loc. cit.*) the preparation of two isomeric acids obtained by the reduction of quinolinic acid. The higher-melting, more sparingly-soluble one he assumes to be the *trans*-modification, the second substance being therefore the *cis*-form.

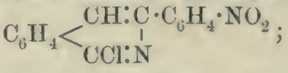
The nitroso-derivative of the *cis*-modification may be made to assume a solid form under suitable conditions; it melts and decomposes at 138—139°. It forms a well-defined strychnine salt, by means of which it may be partially resolved into its optically active components. When the acid in a solution having a distinct rotatory power is converted into the corresponding hexahydroquinolinic acid, all measurable activity is found to have disappeared, but may be brought back by the addition of nitrite to the acidified solution. The melting point of the most active nitroso-acid obtained was 152—153°, or 14° above that of the racemic modification. The partly resolved hexahydroquinolinic acids, when observed in convergent polarised light, were found to exhibit ring-systems unnoticeable in the racemic acid.

Dry bromine is without action on the hydrochloride of the *cis*-acid at 150°; in presence of water, however, action takes place to some extent even at 100°, carbonic anhydride being evolved. The product is readily soluble in water, and melts at 112°, subliming slowly at 100° in beautiful, white needles. Its solubility at 100° precludes the possibility of its identity with ββ-dibromopyridine, with which it agrees in melting point and volatility. A. L.

Derivatives of Isocoumarin, Isocarbostyril, and Isoquinoline. By CHARLES A. HARPER (*Ber.*, 1896, **29**, 2543—2549).—Orthocyanobenzylic cyanide prepared by the method of Gabriel and Otto, from orthocyanobenzylic chloride and potassium cyanide, condenses with metanitrobenzoic chloride in the presence of sodium hydroxide, and on subsequently acidifying the mixture the condensation product. 4-*cyano-3-metanitrophenylisocoumarin*,  $C_6H_4<\begin{matrix}C(CN){:}C\cdot C_6H_4\cdot NO_2,\\ CO\text{——}O\end{matrix}$ is precipitated as a dark-brown powder. It crystallises from glacial acetic acid as a yellow-crystalline powder melting at 210—211°, and is insoluble in ether and light petroleum.

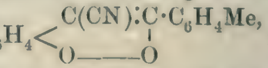
3-*Metanitrophenylisocoumarin*,  $C_6H_4<\begin{matrix}CH{:}C\cdot C_6H_4\cdot NO_2,\\ CO\cdot O\end{matrix}$ is formed on heating the cyano-compound with a mixture of glacial acetic and concentrated hydrochloric acids (1 : 2) in a sealed tube for 2 hours at 180°, and pouring the mixture into water. It melts at 232—233° after recrystallisation from glacial acetic acid.

4-*Cyano-3-metanitrophenylisocarbostyril*,  $C_6H_4<\begin{matrix}C(CN){:}C\cdot C_6H_4\cdot NO_2,\\ CO\text{——}NH\end{matrix}$ is formed when the corresponding isocoumarin is heated in a closed tube for 12 hours at 100° with 20 parts of an alcoholic solution of ammonia; this is insoluble in alcohol and ether, melts above 315°, and is not acted on by phosphorous oxychloride. When heated in a closed tube for $1\frac{1}{2}$ hour at 180° with acetic and hydrochloric acids, 3-*metanitrophenylisocarbostyril* melting at 298—300° is produced; this is readily converted, by heating for 15 minutes on the water bath with phosphorous oxychloride, into 1-*chloro-3-metanitrophenylisoquinoline*,



$$C_6H_4<\begin{matrix}CH{:}C\cdot C_6H_4\cdot NO_2\\ CCl{:}N\end{matrix};$$

the latter crystallises in long, white needles, melting at 220—223°, and is insoluble in ether, cold alcohol, nitrobenzene, and glacial acetic acid.

4-*Cyano-3-paratolylisocoumarin*,  $C_6H_4<\begin{matrix}C(CN){:}C\cdot C_6H_4Me,\\ O\text{———}O\end{matrix}$ is obtained on condensing orthocyanobenzylic cyanide with paratoluic chloride under the same conditions, the best yield being obtained when small quantities are worked with; it is a yellow powder melting at 193—195°.

a-Orthodicyano-β-acetoxyparamethylstilbene,

$$CN\cdot C_6H_4\cdot C(CN){:}C(OAc)\cdot C_6H_4Me,$$

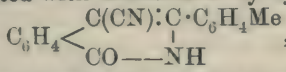
is obtained as an intermediate product in this condensation; it crystallises in rhombic prisms melting at 186—188°.

Paramethyldeoxybenzoinorthocarboxylic acid,

$$C_6H_4Me\cdot CO\cdot CH_2\cdot C_6H_4\cdot COOH,$$

is formed on heating 4-cyano-3-paratolylisocoumarin with glacial acetic and hydrochloric acids in a closed tube at 160°, and melts at 147—148°. It is identical with the compound obtained by Ruhemann from nitroparaxylylidenephthalide.

3-Paratolylisocarbostyril, also previously prepared, is formed when

4-cyano-3-paratolylisocoumarin is heated with ammonia or by hydrolysing *4-cyano-3-paratolylisocarbostyril*,  $C_6H_4<\begin{matrix}C(CN){:}C\cdot C_6H_4Me\\ \vert\\ CO——NH\end{matrix}$, with concentrated hydrochloric and acetic acids, and subsequently eliminating carbonic anhydride. The carbostyril compound is readily formed from the isocoumarin compound on treating it with an alcoholic solution of ammonia. It crystallises in yellow needles and melts at 290—292°.

J. F. T.

Action of Sulphuryl Chloride on Carbazole: Mono- and Di-Chlorocarbazoles.

By GIROLAMO MAZZARA and MANFREDO LAMBERTI-ZANARDI (*Gazzetta*, 1896, **26**, ii, 236—242).—*Monochlorocarbazole*, $C_{12}NH_8Cl$, is prepared by heating a chloroform solution of carbazole on the water bath with sulphuryl chloride; after distilling off the solvent and recrystallising, it is obtained in lustrous, white scales, melting at 192—193°. Its *acetyl*-derivative, $C_{12}H_7ClNAc$, prepared by heating it with acetic anhydride in a sealed tube at 180—200°, crystallises in dull, white needles melting at 124—125°.

Dichlorocarbazole, $C_{12}NH_7Cl_2$, is prepared similarly, and crystallises in white pyramids melting at 202—203°; its *acetyl*-derivative crystallises in opaque, white needles, melting at 185—186°.

Benzoylcarbazole is not chlorinated on heating it with sulphuryl chloride in chloroform solution.

W. J. P.

Conversion of Phenosafranine and Rosinduline into the corresponding Azonium Compounds.

By FRIEDRICH KEHRMANN (*Ber.*, 1896, **29**, 2316—2322).—Further facts are brought forward tending to prove the correctness of the author's theory (*Annalen*, 1896, **290**, 256) of the constitution of the safranines. It is now found that both aposafranine and rosinduline can be readily diazotised, provided the solution be sufficiently strongly acid, and by decomposing these diazo-compounds with alcohol the corresponding azonium bases are produced: in the former case, phenazonium, and in the latter naphthophenazonium.

The method employed is to dissolve aposafranine chloride in a small quantity of water and add first strong sulphuric acid until the colour becomes green, and then a solution of sodium nitrite until it changes to orange-red. Absolute alcohol is then added, and the reaction allowed to proceed 6 hours, after which time the conversion of the diazo-sulphate into phenazonium sulphate is complete. From this, the compound with ferric chloride is precipitated by means of ferric chloride, and recrystallised from glacial acetic acid, from which it separates in fine, red-brown prisms. On adding ammonium carbonate to a solution of this iron salt, iron oxide is precipitated, and the azonium carbonate remains in solution. This solution is rapidly decomposed by ammonia; with sodium hydroxide, aposafranone is produced, and with dimethylaniline, the violet dimethylaposafranine. Strong sulphuric acid dissolves the chloride with the production of a colour similar to that of acetylaposafranine.

Naphthophenazonium is produced in precisely the same way from rosinduline; the compound with ferric chloride crystallises from glacial acetic acid in glistening, metallic green plates which appear red by transmitted light. The solutions of naphthophenazonium show the same coloration as the salts of acetylrosinduline, the colour of the sulphuric acid solutions of the two substances being also similar.

From these facts the author considers that there can no longer be any doubt that both acetylaposafranine and acetylrosinduline are azonium compounds.

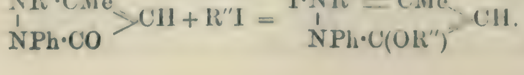
Similarly, phenylisonaphthophenazonium prepared from β-naphthaquinone and phenylorthophenylenediamine gives on solution in concentrated sulphuric acid, a coloration similar to that of acetylisorosinduline. The compound of phenylisonaphthophenazonium with ferric chloride crystallises in glistening, golden leaves. J. F. T.

Constitution of the Safranines. By RUDOLF NIETZKI (*Ber.*, 1896, **29**, 2771—2773. Compare Otto Fischer, Abstr., 1896, i, 628).—The author defends his adherence to the azonium theory of the constitution of the safranines, and criticises the objections of Fischer (*loc. cit.*). M. O. F.

Configuration of Quinone-imide Dyes. By WILHELM VAUBEL (*J. pr. Chem.*, 1896, [2], **54**, 292—304).—The author reviews the theories which have been put forward with regard to the constitution of the dyes of this class, and shows how his configuration for benzene (Abstr., 1894, i, 325) will serve to explain such cases of isomerism as may exist in the class. A. G. B.

Behaviour of Quinone-imide Dyes toward nascent Bromine. By WILHELM VAUBEL (*J. pr. Chem.*, 1896, [2], **54**, 289—291. Compare Abstr., 1895, i, 55).—Phenosafranine combines with 4 atoms of bromine; indazine with 1 atom, rosinduline and rosindone with 1 atom. Meldola's blue readily combines with bromine; methylene blue combines with 1 atom and resorufin with 4 atoms of bromine. A. G. B.

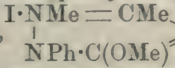
Behaviour of Antipyrine towards Alkyl Haloids. By LUDWIG KNORR (*Annalen*, 1896, **293**, 1—41).—Soon after the discovery of antipyrine, the action of methylic iodide on it at high temperatures was studied, but, instead of the methiodide of the base, a mixture of 1-phenyl-2:3:4-trimethyl-5-pyrazolone (4-methylantipyrine) and 1-phenyl-3:4:4-trimethyl-5-pyrazolone was produced. It is now found that at ordinary temperatures, on application of a moderate heat (60°), antipyrine combines with ethylic iodide, forming a quaternary iodide, isomeric with the methiodide of 1:3:2-phenylmethylethyl-5-pyrazolone (homoantipyrine); the substance, therefore, is not a true ethiodide of antipyrine, being identical with the methiodide derived from the ethyl ether of 3:1-methylphenyl-5-pyrazolone. In view of this fact, the author refers to the new class of compounds as *antipyrine pseudo-alkyliodides*, and expresses the change which results in their production by the equation,

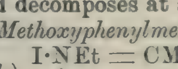


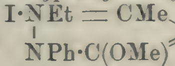
$$\begin{array}{l}\mathrm{NR'\cdot CMe}\\ \mid\\ \mathrm{NPh\cdot CO}\end{array}\!\!>\mathrm{CH} + \mathrm{R''I} = \begin{array}{l}\mathrm{I\cdot NR' = CMe}\\ \mid\\ \mathrm{NPh\cdot C(OR'')}\end{array}\!\!>\mathrm{CH}.$$

This group of quaternary iodides differs from other quaternary iodides in behaviour towards alkalis and also on fusion, antipyrine being regenerated in each case.

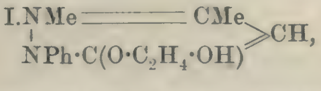
As already stated, the action of methylic iodide on antipyrine at temperatures between 80° and 200° gives rise to a mixture of 4-methylantipyrine and 1-phenyl-3:4:4-trimethyl-5-pyrazolone; these substances are produced in varying quantities according to the conditions observed, a table in the original paper recording the author's results in this direction. It is, moreover, shown that the conversion of the former subtance, which constitutes the primary product of action, into 1-phenyl-3:4:4-trimethyl-5-pyrazolone, does not depend on molecular rearrangement, but arises from the further action of methylic iodide.

5:1:3-*Methoxyphenylmethylpyrazole methiodide* (*antipyrine pseudo-methiodide*),  $\left.\begin{array}{l}\mathrm{I{\cdot}NMe = CMe}\\ \quad|\\ \mathrm{NPh{\cdot}C(OMe)}\end{array}\right>\mathrm{CH}$, is obtained when antipyrine or 5:1:3-methoxyphenylmethylpyrazole (Abstr., 1895, i, 397) remains with excess of methylic iodide in closed vessels for several days at 60°; it decomposes and melts somewhat indefinitely at 130°, yielding antipyrine and methylic iodide. It separates from a mixture of ether and alcohol in crystals which belong to the monoclinic system, and has a sp. gr. = 1·580 at 22°. The *platinochloride* of the methochloride crystallises in orange needles, and decomposes about 210°.

5:1:3-*Ethoxyphenylmethylpyrazole methiodide* (*antipyrine pseudo-ethiodide*),  $\left.\begin{array}{l}\mathrm{I{\cdot}NMe = CMe}\\ \quad|\\ \mathrm{NPh{\cdot}C(OEt)}\end{array}\right>\mathrm{CH}$, is obtained from antipyrine and ethylic iodide, or from 3:1-methylphenyl-5-ethoxypyrazolone and methylic iodide; it forms monoclinic crystals having a sp. gr. = 1·583 at 17·5°, and melts and decomposes at 113—116°, yielding antipyrine and ethylic iodide. The *platinochloride* of the corresponding methochloride melts and decomposes at about 198°.

5:1:3-*Methoxyphenylmethylpyrazole ethiodide* (*homoantipyrine-pseudo-methiodide*),  $\left.\begin{array}{l}\mathrm{I{\cdot}NEt = CMe}\\ \quad|\\ \mathrm{NPh{\cdot}C(OMe)}\end{array}\right>\mathrm{CH}$, is obtained from the higher homologue of antipyrine, 1:3:2-phenylmethylethyl-5-pyrazolone and methylic iodide; it melts at 114—115°, and yields methylic iodide and homoantipyrine. Boiling caustic soda also regenerates homoantipyrine, which distinguishes the original substance from the isomeric antipyrine pseudo-ethiodide. The *platinochloride* of the corresponding ethochloride crystallises in orange prisms, and decomposes at about 195°.

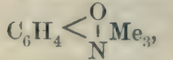
5-*Hydroxyethoxy*-1:3-*phenylmethylpyrazole methiodide*,



$$\left.\begin{array}{l}\mathrm{I.NMe = = = CMe}\\ \quad|\\ \mathrm{NPh{\cdot}C(O{\cdot}C_2H_4{\cdot}OH)}\end{array}\right>\mathrm{CH},$$

is prepared from 5-hydroxyethoxy-1:3-phenylmethylpyrazole (*loc. cit.*), and melts at 129—130°. The *platinochloride* of the methochloride crystallises in orange prisms, and melts at 202°.

The unexpected result of treating antipyrine with methylic iodide at common temperatures recalls the behaviour of phenolbetaïnes towards this agent; thus trimethylphenolammonium,

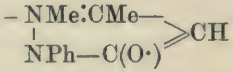

$C_6H_4<\begin{array}{c}O\\|\\N\end{array}Me_3$,

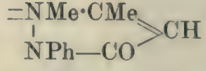
described by Griess (*Ber.*, 13, 246), yields with potash and methylic iodide trimethylanisoïlammonium iodide, $OMe\cdot C_6H_4\cdot NMe_3I$, which is derivable, under the same conditions, from dimethylamidoanisoïl,

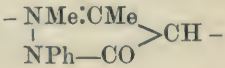
$$OMe\cdot C_6H_4\cdot NMe_2.$$

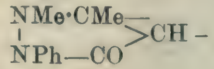
This similarity of behaviour suggests a phenolbetaïne formula for antipyrine, but on comparing the substance more closely with the betaïne of orthohydroxyphenyltrimethylammonium hydroxide it is found that the analogy is not sustained, for whilst the latter compound has an alkaline action in aqueous solution, and is not precipitated by alkalis, antipyrine is neutral, and separates from its solution on the addition of alkalis; moreover, orthohydroxyphenyltrimethylammonium hydroxide is converted into orthodimethylamidoanisoïl when distilled, antipyrine undergoing this treatment without change. Characteristic differences also present themselves when the alkylic iodide additive products of both compounds are submitted to comparison.

Some interesting observations are made regarding the theoretical aspect of these results, and the author points out that the phenomena described may be traced to the nitrogen atom 2, which is alternatively ter- and quinque-valent, whilst the behaviour of antipyrine is best explained on the hypothesis that it assumes one of the four modifications,

I

$\begin{array}{l}-NMe\colon CMe-\\ \;\;|\\ NPh-C(O\cdot)\end{array}>CH$

II

$\begin{array}{l}=NMe\cdot CMe\\ \;\;|\\ NPh-CO\end{array}>CH$

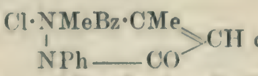
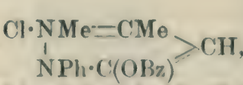
III

$\begin{array}{l}-NMe\colon CMe\\ \;\;|\\ NPh-CO\end{array}>CH-$

IV

$\begin{array}{l}NMe\cdot CMe-\\ \;\;|\\ NPh-CO\end{array}>CH-$

according to the circumstances in which it is placed. This view finds support in the behaviour of the substance towards bromine (Abstr., 1887, 603), which occupies the positions 3:4. Towards methylic iodide, at temperatures above 80°, antipyrine behaves as a compound having the structure represented by II and III, whilst the form I is assumed when the substance is treated with methylic iodide at the ordinary temperature.
M. O. F.

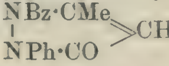
Additive Product of Antipyrine and Benzoic Chloride. By Ludwig Knorr and Paul Rabe (*Annalen*, 1896, **293**, 42—48).—In accordance with the unsaturated character of antipyrine (compare foregoing abstract), the substance forms an additive product with benzoic chloride, but it is not decided at present whether the benzoyl group is attached to oxygen or nitrogen.

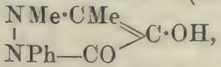
Antipyrine benzochloride,

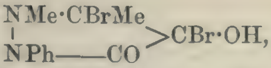

$\begin{array}{l}Cl\cdot NMeBz\cdot CMe\\ \;\;\;\;|\\ \;\;NPh-\!\!-CO\end{array}>CH$ or

$\begin{array}{l}Cl\cdot NMe=CMe\\ \;\;\;\;|\\ \;\;NPh\cdot C(OBz)\end{array}>CH$,

is obtained on adding freshly distilled benzoic chloride (140 parts) to antipyrine (188 parts) dissolved in benzene (2,000 parts); it is readily soluble in water, alcohol, acetone, and chloroform, and insoluble in ether, petroleum, and benzene. The substance crystallises slowly in prisms on adding benzene to the solution in chloroform, and melts at 129—130°, forming a colourless liquid, which becomes red and evolves gas at 180°. The benzochloride is much more sensitive towards alkalis than the pseudo-alkyliodides, and is also slowly decomposed by cold water, yielding antipyrine, whilst the pseudo-alkyliodides are indifferent towards boiling water.

When heated at 180°, antipyrine benzochloride gives rise to benzoic and methylic chlorides, antipyrine, and Nef's benzoylphenylmethyl-5-pyrazolone, which melts at 75° (Abstr., 1892, 146); only one-third of the original substance, however, breaks up in such a manner as to yield methylic chloride and benzoylphenylmethylpyrazolone. The corresponding benzoiodide, which according to Stolz (private communication) is obtained by the action of methylic iodide on benzoylphenylmethylpyrazolone dissolved in benzene, yields the last-named substance in quantity amounting to 75 per cent. when heated; its identity with Nef's compound is established by the production, from both preparations, of the same *picrate*, which melts at 119—120°, and has a sp. gr. = 1·42 at 12°.

According to these results, the benzoyl group occupies the same position in antipyrine benzochloride as in benzoylphenylmethylpyrazolone; if Nef's formula for the latter substance,  $\begin{array}{l} \mathrm{NBz{\cdot}CMe} \\ \quad | \\ \mathrm{NPh{\cdot}CO} \end{array}\!>\!\mathrm{CH}$, is correct, the addition of benzoic chloride to antipyrine proceeds in a sense different from the addition of alkylic iodides, a course which the author considers improbable. M. O. F.

4-Hydroxy-1-phenyl-2:3-dimethyl-5-pyrazolone (4-hydroxyantipyrine). By LUDWIG KNORR and ROBERT PSCHORR (*Annalen*, 1896, **293**, 49—55).—4-*Hydroxyantipyrine*,  $\begin{array}{l} \mathrm{NMe{\cdot}CMe} \\ \quad | \\ \mathrm{NPh{-}CO} \end{array}\!>\!\mathrm{C{\cdot}OH}$, is obtained by heating equal quantities of 4-hydroxy-1:3-phenylmethyl-5-pyrazolone and methylic iodide with methylic alcohol for 8 hours at 110°, and treating the product with sulphurous acid; it is also formed when 4-bromantipyrine is treated with excess of hot, concentrated potash. The substance is readily soluble in alcohol, chloroform, benzene, and hot water, but only sparingly so in ether and petroleum; it crystallises in colourless needles, and melts at 182°. Hydroxyantipyrine is phenolic in character, and the *sodium* derivative is decomposed by carbonic anhydride. The *methyl ether* crystallises from ether and light petroleum in small plates, and melts at 75°; the *ethyl ether* crystallises from petroleum of high boiling point in small needles, and melts at 60°. The *benzoate* crystallises from toluene and melts at 139°.

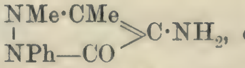
4-Hydroxyantipyrine *dibromide*,  $\begin{array}{l} \mathrm{NMe{\cdot}CBrMe} \\ \quad | \\ \mathrm{NPh{-\!-}CO} \end{array}\!>\!\mathrm{CBr{\cdot}OH}$, separates in colourless needles from the chloroform solution on the addition of ether, and melts at 218—220°; the action of water regenerates hydroxyantipyrine. M. O. F.

Reduction of Nitroso-antipyrine. By LUDWIG KNORR and THEODOR GEUTHER (*Annalen*, 1896, **293**, 55—57).—4-Amido-antipyrine *hydrochloride* is obtained by reducing nitroso-antipyrine or nitro-antipyrine (Abstr., 1892, 730); it forms colourless crystals, and melts, decomposing, at 231°. The *platinochloride* forms bright yellow crystals.

Antipyrine-azo-β-naphthol is produced when an alkaline solution of β-naphthol is added to diazotised amido-antipyrine, and crystallises from glacial acetic acid in red needles.

Nitroso-antipyrine *hydrochloride* crystallises in small, yellow needles, and melts and decomposes at 80°; it is an unstable substance, gradually losing hydrogen chloride when exposed to air; water reconverts it into nitroso-antipyrine. M. O. F.

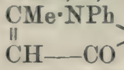
4-Amidoantipyrine. By LUDWIG KNORR and FRIEDRICH STOLZ (*Annalen*, 1896, **293**, 58—69).—The method described in the foregoing abstract is not suited for the production of 4-amidoantipyrine in considerable quantity; it is most conveniently prepared by reducing nitroso-antipyrine dissolved in alcohol with zinc dust and glacial acetic acid, and when the reddish-violet liquid has become pale yellow, converting the base into the benzylidene derivative by means of benzaldehyde.

4-*Amido-antipyrine*,  $\begin{matrix}\mathrm{NMe{\cdot}CMe}\\ | \\ \mathrm{NPh{-}CO}\end{matrix}\!\!>\!\mathrm{C{\cdot}NH_2}$, crystallises from benzene in minute, pale yellow needles, and melts at 109°; it is sparingly soluble in ether, but dissolves readily in benzene, alcohol, and water. The *sulphate* dissolves with difficulty in alcohol, and separates from water in plates melting at 215°; the *picrate* crystallises in leaflets, and melts at 144°. The *benzylidene* derivative crystallises from alcohol in lustrous, yellow leaflets, and melts at 173°; the *hydroxybenzylidene* and *metanitrobenzylidene* derivatives melt at 194° and 213° respectively, whilst the *cinnamylidene* derivative melts at 160°. Amido-antipyrine forms a *compound*, $C_{17}H_{21}N_3O_3$, with ethylic acetoacetate, which crystallises from dilute alcohol in colourless needles, and melts at 158—160°; the *compound*, $C_{17}H_{17}N_3O_5$, obtained from amido-antipyrine and pyruvic acid, crystallises from alcohol in bright yellow, lustrous prisms, and melts at 170°. The *acetyl* derivative of amido-antipyrine crystallises from toluene, and melts at 197°, whilst the *formyl* derivative melts at 189°; the *dibenzoyl* derivative crystallises from alcohol, and melts at 188°. *Antipyrylcarbamide* crystallises in leaflets and melts at 245°, whilst *symmetrical diantipyrylthiocarbamide* melts and decomposes at 248°; the *urethane* derivative crystallises from dilute alcohol and melts at 206°.

4-*Dimethylamido-antipyrine* separates from a mixture of petroleum and ethylic acetate in colourless crystals, and melts at 108°; the *methiodide* crystallises slowly from water, and melts indefinitely at 220°.

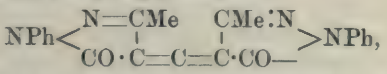
Diazo-antipyrine chloride is obtained in solution by the action of nitrous acid on amido-antipyrine ; when sodium acetate is added to a mixture of the substance with aniline acetate, *diazo-antipyrineamidobenzene* separates as a yellow precipitate, and decomposes at 136—137°. Diazo-antipyrine combines with phenols forming azo-colouring matters. The *antipyrylhydrazone* of 1:3-phenylmethyl-4:5-ketopyrazolone is obtained on adding methylphenylpyrazolone in glacial acetic acid to a solution of diazo-antipyrine chloride ; it crystallises from alcohol in beautiful red needles, and decomposes at 200—205°.

M. O. F.

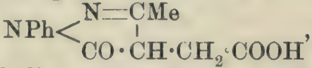
Pyrazolone Derivatives. By R. HIMMELBAUER (*J. pr. Chem.*, 1896, [2], 54, 177—214. Compare Abstr., 1895, i, 570.)—*Methylic* 1:3-*phenylmethyl-5-pyrazolone-2-carboxylate,*  $\left.\begin{matrix}\mathrm{CMe{\cdot}NPh}\\ \| \\ \mathrm{CH{-\!-\!-}CO}\end{matrix}\right>\mathrm{N{\cdot}COOMe}$, is prepared by dissolving the pyrazolone (1 mol.) in cold sodium hydroxide (1 mol.) solution and adding methylic chlorocarbonate (1 mol.) ; after 12 hours, during which time the containing vessel must be frequently shaken, the lower, oily layer is dissolved in ether, dried by lime and evaporated. The yield is 91·5 per cent. of that calculated. The compound is also formed in the absence of alkali, but a high temperature is then necessary. It forms brilliant, well-built, compact crystals, melts at 52°, and is freely soluble in all the usual solvents, except water, mineral acids, and alkalis. The ease with which the carboxymethyl group can be eliminated by hydrolysing agents is characteristic of this salt. Ferric chloride gives no coloration with the alcoholic solution of the salt, nor does nitrous acid react with it to form a nitroso-compound ; with bromine, it yields an additive product. When heated at 180° and finally at 250° the methylic carboxylate loses carbonic anhydride, 1:2:3-phenyldimethyl-5-pyrazolone (antipyrine) and 1:3-phenylmethylmethoxypyrazole (Knorr, Abstr., 1895, i, 397) being formed.

Ethylic 1:3-phenylmethyl-5-pyrazolone-2-carboxylate has been already described (Abstr., 1895, i, 570) ; at 300° it loses carbonic anhydride and if the hot residue be added to absolute alcohol, crystals of carbo-bis-1:3-phenylmethyl-5-pyrazolone separate, on cooling (see below). The mother liquor from these crystals, when evaporated and distilled with steam, yields 1:3-phenylmethyl-5-ethoxypyrazole (Abstr., 1895, i, 396), which may be extracted by ether ; the aqueous solution contains 1:2:3-phenylethylmethyl-5-pyrazolone (Aldrich, Diss. Jena, 1892, 20). The *platinochloride* (with $2H_2O$) and the *nitroso*-derivative were prepared.

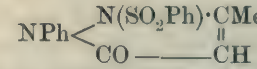
Carbo-bis-1:3-*phenylmethyl-5-pyrazolone,*



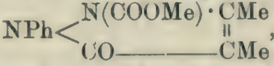
$$\mathrm{NPh}\left<\begin{matrix}\mathrm{N{=\!=}CMe} & & \mathrm{CMe{:}N} \\ | & & | \\ \mathrm{CO{\cdot}C{=\!=}} & \mathrm{C} & \mathrm{{=\!=}C{\cdot}CO{-\!-}}\end{matrix}\right>\mathrm{NPh},$$

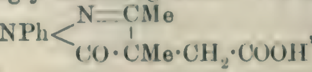
is obtained as already stated, and also when carbonyl chloride is passed into melted phenylmethylpyrazolone (antipyrine) at 150—180° ; the mass is powdered, washed with dilute acid, and fractionally crystallised from absolute alcohol, in which the carbo-compound is less soluble than the condensation product mentioned below. It crystallises in white, silky needles, melts at 235° and is insoluble in dilute mineral acids and alkalis, sparingly soluble in alcohol and benzene, more freely in glacial acetic acid and phenol; it can be distilled under diminished pressure. The *condensation* product which crystallises from the mother liquor of the foregoing compound is the main product of the action; it forms brick-red crystals, does not melt at 280° and is easily soluble in alkalis and fairly soluble in hot alcohol, glacial acetic acid, phenol and strong hydrochloric acid. 1:3-Phenylmethyl-5-pyrazolone-4-acetic acid,  $\mathrm{NPh}<\begin{array}{l}\mathrm{N{=}CMe}\\ \quad |\\ \mathrm{CO\cdot CH\cdot CH_2\cdot COOH}\end{array}$, has been prepared by the action of ethylic acetosuccinate on phenylhydrazine (Knorr and Blank, Abstr., 1884, 1380); it is now obtained by heating phenylmethylpyrazolone, dissolved in alkali, with an equivalent of sodium chloracetate. When heated at 200°, it loses carbonic anhydride and yields 1:3:4-phenyldimethyl-5-pyrazolone (Knorr., Abstr. 1887, 601); this melts at 130°.

2:1:3-Benzoylphenylmethylpyrazolone has been described by Nef (Abstr., 1892, 146); it is debenzoylised when treated with phenylhydrazine or hydroxylamine.

1:2:3-*Phenylsulphonemethyl-5-pyrazolone*,  $\mathrm{NPh}<\begin{array}{l}\mathrm{N(SO_2Ph)\cdot CMe}\\ \mathrm{CO}\text{———}\mathrm{CH}\end{array}$, from benzenesulphonic chloride and commercial phenylmethylpyrazolone, melts at 91—92° and dissolves freely in ether, alcohol and benzene but not in water.

1:2:3-*Phenylbenzylmethyl-5-pyrazolone* crystallises in needles, melts at 134—136° and has the same solubility as commercial pyrazolone. The substance obtained by Knorr by reducing 1:3:4-phenylmethylbenzylidenepyrazolone (Abstr., 1887, 602) has the formula $C_{21}H_{20}N_3O_2$ and melts at 157°; it is therefore not the benzyl derivative.

2:1:3-*Acetylphenylmethyl-5-pyrazolone*, from phenylmethylpyrazolone and acetic chloride in benzene solution, is a pale yellow oil, boils at 200° (10 mm.) and is insoluble in water, alkalis and acids, but soluble in the usual organic solvents. *Methylic* 1:3:4-*phenyldimethyl-5-pyrazolone-2-carboxylate*  $\mathrm{NPh}<\begin{array}{l}\mathrm{N(COOMe)\cdot CMe}\\ \mathrm{CO}\text{————}\mathrm{CMe}\end{array}$, is obtained by shaking the pyrazolone with methylic chlorocarbonate in an alkaline solution; it is an oil which solidifies at low temperatures and decomposes when distilled, even in a vacuum; most solvents dissolve it, except water, acids and alkalis. The distillate from this salt yields 1:3:4-phenyldimethyl-5-methoxypyrazole (Abstr., 1895, i, 397) when distilled with steam. The original residue of the distillation also contains 1:2:3:4-phenyltrimethyl-5-pyrazolone (m. p. 82°).

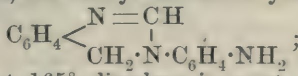
1:3:4-*Phenyldimethyl-5-pyrazolone-2-acetic acid* is prepared by heating sodium chloracetate with the pyrazolone in alkaline solution for 2 minutes; it crystallises in white needles (with $1H_2O$), melts at 102°, and loses its water of crystallisation at 115°; it dissolves easily in alcohol and ether, and sparingly in boiling water. 1:3:4-*Phenyldimethyl-5-pyrazolone-4-acetic acid*,  $\mathrm{NPh}<\begin{array}{l}\mathrm{N{=}CMe}\\ \quad |\\ \mathrm{CO\cdot CMe\cdot CH_2\cdot COOH}\end{array}$, is formed if the heating be continued for 25—30 minutes in a reflux apparatus; it melts at 190°. A. G. B.

Syntheses of Quinazolines. By CARL PAAL (*J. pr. Chem.*, 1896, [2], **54**, 258—264. Compare Abstr., 1894, i, 210).—An introduction to the four succeeding papers. A. G. B.

Synthesis of 3′-Orthamidophenyldihydroquinazoline. By CARL PAAL and GEO KROMSCHRÖDER (*J. pr. Chem.* 1896, [2], **54**, 265—270).—*Orthonitrobenzylorthonitraniline*, $NO_2\cdot C_6H_4\cdot CH_2\cdot NH\cdot C_6H_4\cdot NO_2$, is prepared by heating orthonitrobenzylic chloride (1 mol.) with orthonitraniline (2 mols.) in an oil bath for 2 hours at 130°, and the cooled mass is treated with hot, dilute hydrochloric acid, when the new compound is left undissolved. It crystallises in laminæ which have a golden lustre, melts at 137°, and dissolves sparingly in alcohol, but more freely in benzene and glacial acetic acid; it has no basic properties.

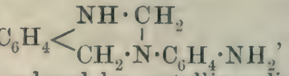
Orthonitrobenzylorthophenylenediamine,

$$NO_2\cdot C_6H_4\cdot CH_2\cdot NH\cdot C_6H_4\cdot NH_2,$$

is obtained as its hydrochloride when orthonitrobenzylic chloride (1 mol.) and orthophenylenediamine (1 mol.) are heated together in strong alcoholic solution; it crystallises in red needles, melts at 115°, and dissolves in alcohol, ether, glacial acetic acid, ethylic acetate, chloroform and benzene. The *hydrochloride*, $C_{13}H_{13}N_3O_2,HCl$, crystallises in white needles and melts at 202°. The *formyl*-derivative, $NO_2\cdot C_6H_4\cdot CH_2\cdot N(C_6H_4\cdot NH_2)\cdot CHO$, is formed when the phenylenediamine is heated with anhydrous formic acid; it crystallises in thick, pale yellow tablets, melts at 158°, and dissolves in most of the usual organic solvents; it is somewhat basic. A second compound obtained at the same time was found to melt at 138°, but has not been further investigated. By reduction in alcoholic solution by means of tin and hydrochloric acid, the formyl-derivative yields *3′-orthamidophenyldihydroquinazoline*,  $C_6H_4\Big<\begin{matrix}N{=}CH\\ |\\ CH_2\cdot N\cdot C_6H_4\cdot NH_2\end{matrix}$; this forms pale yellow crystals, melts at 165°, dissolves in most organic solvents, save light petroleum, and is strongly basic; the *hydrochloride* is very unstable; the *picrate* (m. p. 184°) and the *oxalate* (with $2H_2O$) are described. A. G. B.

Synthesis of 3-Paramidophenyldihydroquinazoline. By CARL PAAL and H. POLLER (*J. pr. Chem.*, 1896, [2], **54**, 271—277).—*Orthonitrobenzylparanitraniline* is prepared from orthonitrobenzylic chloride and paranitraniline (compare preceding abstract); it crystallises in large laminæ, with a bronze lustre, melts at 202°, and has no basic properties. When reduced by zinc dust and glacial acetic acid at a temperature not exceeding 40°, it yields *orthamidobenzylparaphenylenediamine*, $NH_2\cdot C_6H_4\cdot CH_2\cdot NH\cdot C_6H_4\cdot NH_2$, this crystallises in nearly colourless laminæ, and melts at 114°; the *hydrochloride* and the *oxalate* were obtained.

Formorthonitrobenzylparanitranilide, obtained by heating the nitraniline with anhydrous formic acid, crystallises in thick, short, yellowish prisms, melts at 155—156°, and dissolves sparingly in alcohol and more freely in benzene. When suspended in alcohol and heated with granulated tin in a reflux apparatus, strong hydrochloric acid being added in small portions at a time, the formyl-derivative is reduced to *3′-paramidophenyldihydroquinazoline*, which crystallises in the form of its *stannochloride*, $C_{14}H_{13}N_3,2HCl,2SnCl_2$; the double salt is decomposed in the usual manner whereby the quinazoline is obtained in flat, white, feathery needles. It melts at 175°, and is freely soluble in dilute mineral acids, alcohol and chloroform, more sparingly in ethylic acetate and benzene, and hardly at all in water and light petroleum. The *hydrochloride*, $C_{14}H_{13}N_3,2HCl,2H_2O$, *hydrobromide*, $C_{14}H_{13}N_3,2HBr$, *platinochloride*, *oxalate* (m. p. 237°), and *picrate* (m. p. 199°) are described.



3′-Paramidophenyltetrahydroquinazoline, $C_6H_4<\begin{matrix}NH\cdot CH_2\\ \vert\\ CH_2\cdot N\cdot C_6H_4\cdot NH_2\end{matrix}$, is produced when the dihydroquinazoline is reduced by metallic sodium in hot alcoholic solution; it crystallises in small, flat, white needles, melts at 138°, and dissolves freely in alcohol and ethylic acetate, more sparingly in ether, chloroform and benzene, but hardly at all in water or light petroleum; the solutions become violet on exposure to the air. The *hydrochloride*, *platinochloride*, *oxalate*, and *picrate* were obtained.

A. G. B.

Synthesis of 3′-Orthanisyldihydroquinazoline. By CARL PAAL and WILHELM SCHILLING (*J. pr. Chem.*, 1896, [2], **54**, 277—283).

—*Orthonitrobenzylorthanisidine*, $NO_2\cdot C_6H_4\cdot CH_2\cdot NH\cdot C_6H_4\cdot OMe$.—When orthonitrobenzylic chloride (1 mol.) and orthanisidine (2 mols.) are heated together in alcoholic solution which is afterwards mixed with sodium acetate and acetic acid, diluted with water and extracted by ether, two compounds are obtained; they are separated by dissolving in alcohol the residue left on evaporation of the ether and adding alcoholic hydrogen chloride and ether, whereby white needles of orthonitrobenzylorthanisidine *hydrochloride*, $C_{14}H_{14}N_2O_3,HCl$ (m. p. 158°) are precipitated. The base itself, which may be obtained free from the second compound by heating orthonitrobenzylic chloride with orthanisidine in alcoholic soda solution, crystallises in lustrous, red prisms or tables with oblique ends; it melts at 80°. The second compound referred to above is *bisorthonitrobenzylorthanisidine*,

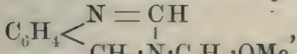
$$[NO_2\cdot C_6H_4\cdot CH_2]_2\colon N\cdot C_6H_4\cdot OMe,$$

and crystallises from the filtrate from the foregoing hydrochloride in small, thick, very yellow tablets which dissolve moderately well in hot alcohol and more freely in glacial acetic acid and benzene; it melts at 117° and has no basic properties.

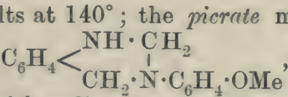
Orthamidobenzylorthanisidine, $NH_2\cdot C_6H_4\cdot CH_2\cdot NH\cdot C_6H_4\cdot OMe$, is prepared by reducing the nitro-compound with zinc dust in glacial acetic acid at a temperature not exceeding 30°; the base is extracted by ether from the solution, and precipitated by dilution and addition of excess of alkali. It crystallises in large, white, flat needles and melts at 95°.

Formorthonitrobenzylorthanisidide,

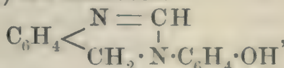
$$NO_2\cdot C_6H_4\cdot CH_2\cdot N(C_6H_4\cdot OMe)\cdot CHO,$$

prepared by heating the nitro-compound with anhydrous formic acid, crystallises in large, well-formed, colourless, oblique prisms, and melts at 82°. By reduction with zinc dust in cold glacial acetic acid solution, it yields the corresponding *amido*-derivative and hydroquinazoline. The former crystallises from the ethereal extract of the solution rendered alkaline, in aggregates of white needles and melts at 98°; it dissolves in dilute mineral acids, and when these solutions are heated it is converted into the hydroquinazoline. *3′-Anisyldihydroquinazoline*,  $C_6H_4<\begin{array}{l}N=CH\\ \quad\;|\\ CH_2\cdot N\cdot C_6H_4\cdot OMe\end{array}$, is best obtained by reducing formorthonitrobenzylorthanisidide with tin and hydrochloric acid in alcoholic solution; it is an oil, and is easily soluble in the usual organic solvents. The *hydrochloride*, $C_{15}H_{14}N_2O,HCl$, crystallises in white, fan-shaped laminæ or needles and melts at 128°; the *stannochloride*,

$$C_{15}H_{14}N_2O,HCl,SnCl_2$$

forms large, colourless tables and melts at 140°; the *picrate* melts at 197°. *3′-Anisyltetrahydroquinazoline*,  $C_6H_4<\begin{array}{l}NH\cdot CH_2\\ \quad\;\;|\\ CH_2\cdot N\cdot C_6H_4\cdot OMe\end{array}$, formed by reducing the dihydroquinazoline with sodium in alcoholic solution, crystallises in white, stellate needles, melts at 96° and is freely soluble in ether, alcohol, ethylic acetate, and benzene. A. G. B.

Synthesis of 3′-Paranisyldihydroquinazoline. By Carl Paal and Wilhelm Schilling (*J. pr. Chem.*, 1896, [2], **54**, 283—288).—*Orthonitrobenzylparanisidine*, from orthonitrobenzylic chloride and paranisidine (compare preceding abstract), crystallises in large, scarlet laminæ, melts at 73°, and is insoluble in water, sparingly soluble in light petroleum, but easily in most other organic solvents; the *hydrochloride*, $C_{14}H_{14}N_2O_3,HCl$, forms white needles, melting at 185°. When heated with formic acid, the base is converted into *formorthonitrobenzylparanisidide*, which crystallises in short, colourless, transparent prisms, melts at 69° and is freely soluble in warm carbon bisulphide, ether, alcohol, glacial acetic acid, ethylic acetate, and benzene; it has no basic properties. The best reducing agent to convert the formyl-derivative into the quinazoline is zinc dust and hydrochloric acid in an alcoholic solution; *3′-paranisyldihydroquinazoline* crystallises in thick, transparent tablets, melts at 115°, and dissolves easily in alcohol, ethylic acetate, and benzene; the *hydrochloride*, $C_{15}H_{14}N_2O,HCl$, crystallises in slender, white needles and in stellate prisms, and melts at 237°; the *zincochloride*, the *platinochloride*, and the *picrate* (m. p. 181°) are described.

Parahydroxyphenyldihydroquinazoline,  $C_6H_4<\begin{array}{l}N=CH\\ \quad\;|\\ CH_2\cdot N\cdot C_6H_4\cdot OH\end{array}$, is formed by heating the anisyldihydroquinazoline with five times its weight of strong hydrobromic acid in a sealed tube for 1 hour at 130°

It crystallises in hard, yellowish prisms, melts at 235° and dissolves freely in dilute mineral acids and caustic alkalis, but only sparingly in most organic solvents.

3′-Paranisyltetrahydroquinazoline, obtained from the dihydro-base by the action of sodium in alcohol, crystallises in nacreous laminæ, melts at 134°, and dissolves freely in most hot organic solvents.

A. G. B.

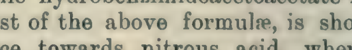
Condensation of Benzaldehyde with Ethylic Acetoacetate in presence of Aromatic Amines.

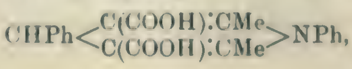
By Bronislaw Lachowicz (*Monatsh.*, 1896, 17, 343—360).—*Ethylic hydrobenzimidoacetoacetate*, $CHPh\colon N\cdot CHPh\cdot NH\cdot CMe\colon CH\cdot COOEt$

$$(\text{or } CHPh\colon N\cdot CHPh\cdot N\colon CMe\cdot CH_2\cdot COOEt)$$

is obtained when a mixture of 2 molecular proportions of ethylic acetoacetate and 1 of benzaldehyde is allowed to remain during about 12 hours at the ordinary temperature with excess of dilute alcoholic ammonia; it is deposited in long, colourless needles, and crystallises in thick prisms, melting at 129°; it is insoluble in water, but dissolves readily in alcohol and benzene, and is also dissolved by acids, but is reprecipitated on adding an alkali. It is not affected by boiling caustic potash, but, when heated with hydrochloric acid it breaks down with formation of benzaldehyde and ammonium chloride; it is also slowly decomposed by boiling alcohol. When heated with aniline or phenylhydrazine, it evolves ammonia, and benzylideneanilide or benzylidenehydrazone are produced. It reacts with warm ethylic acetoacetate, yielding Schiff and Puliti's ethylic phenylhydrolutidinedicarboxylate (Abstr., 1883, 1151); the production of this substance is probably preceded by the formation of an unstable, intermediate compound of the structure $CHPh(NH\cdot CMe\colon CH\cdot COOEt)_2$.

That the constitution of ethylic hydrobenzimidoacetoacetate is most probably represented by the first of the above formulæ, is shown by the behaviour of the substance towards nitrous acid, whereby a nitroso-compound is produced. It may be directly synthesised by allowing a solution of molecular proportions of ethylic acetoacetate and hydrobenzamide in alcohol to remain during 48 hours, when benzaldehyde and the above compound are produced in molecular proportion.

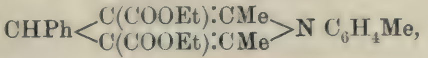
Benzylideneanilide and ethylic acetoacetate dissolved in alcohol react at ordinary temperatures, and, after a fortnight, the addition of water causes the precipitation of a new compound, probably *ethylic diphenyldihydrolutidinedicarboxylate*,  $CHPh<\begin{matrix}C(COOEt)\colon CMe\\C(COOEt)\colon CMe\end{matrix}>NPh$; this crystallises in colourless prisms, showing a weak, pale blue fluorescence, melts at 159—160°, and dissolves readily in alcohol, but only sparingly in ether or light petroleum. It is also produced when ethylic anilacetoacetate is warmed with a mixture of benzaldehyde and ethylic acetoacetate. It is slowly hydrolysed by alkalis, but when boiled with alcoholic potash during 12—14 hours, the liquid, on the addition of acetic acid, deposits 1:4-*diphenyldihydrolutidine*-3:5-*dicarboxylic acid*,



$$CHPh<\begin{matrix}C(COOH)\colon CMe\\C(COOH)\colon CMe\end{matrix}>NPh,$$

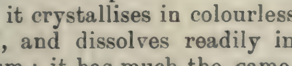
which crystallises from alcohol in yellow, flat, microscopic prisms, and melts at 165°, evolving carbonic anhydride.

Ethylic 1:4-*paratolylphenyldihydrolutidine*-3:5-*dicarboxylate*,



$$CHPh<\begin{matrix}C(COOEt):CMe\\C(COOEt):CMe\end{matrix}>N\ C_6H_4Me,$$

is obtained when paratoludine is substituted for aniline in the above action; it crystallises in colourless leaflets, melts without decomposing at 133°, and dissolves readily in alcohol, ether, benzene and light petroleum; it has much the same character as the former compound, but when treated with potash under the conditions requisite for the complete hydrolysis of that substance, yields the intermediate *monoethylic* salt, $C_{24}H_{25}O_4N$; the latter crystallises from alcohol in colourless leaflets, and melts and decomposes at 160°.

A mixture of ethylic acetoacetate and benzidine does not readily form a condensation product with phenylhydrazine in the cold, benzylidenehydrazone being invariably produced; if, however, the hydrazone of ethylic acetoacetate is first prepared and mixed with benzaldehyde, interaction takes place at the ordinary temperature with formation of a *substance* which separates, after 48 hours, in the form of highly-dispersive rhombohedral prisms. The same compound is produced from a mixture of benzaldehyde and 1:3:5-phenylmethylpyrazolone, and is doubtless 4-*benzylidene-bis*-1:3:5 *phenylmethylpyrazolone*,  $CHPh\left(CH<\begin{matrix}CO-NPh\\ \vert\\ CMe:N\end{matrix}\right)_2$. It crystallises from chloroform and melts to a red liquid at 154°, but after dissolution in ethylic alcohol yields crystals containing alcohol ($\frac{1}{2}$ mol.); these melt at 165°, and after liquefaction yield the same substance; the crystals from methylic alcohol also contain the solvent (1 mol.), and melt at 148°, evolving the alcohol. The pyrazolone dissolves readily in alcoholic hydrochloric acid, but in a short time a crystalline *substance*,

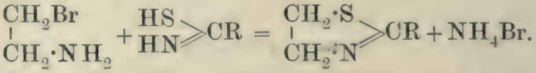
$$C_{27}H_{24}O_2N_4,HCl + EtOH,$$

is formed which is sparingly soluble in alcohol, and melts and decomposes at 232°. It also dissolves readily in aqueous ammonia, the solution in a short time depositing a *compound*, $C_{27}H_{24}O_2N_4,NH_3 + \frac{1}{2}H_2O$, which forms rose-coloured, highly-dispersive, quadratic prisms, and melts and decomposes at 166°; this substance is dissolved by alcohol, and the pyrazolone may be recovered from the resulting solutions. Analogous compounds are also obtained when other amines are employed; thus a mixture of piperidine and alcohol at once dissolves the pyrazolone, and the liquid subsequently deposits a *substance*,

$$C_{27}H_{24}O_2N_4,C_5H_{11}N + \tfrac{1}{2}EtOH,$$

in the form of long, colourless prisms, which melt and decompose at 196°. A dilute alkaline solution of 4-benzylidenebis-1:3:5-phenylmethylpyrazolone yields an amorphous precipitate when mixed with salts of the heavy metals, and its alcoholic solution gives a deep brownish-red coloration with ferric chloride. A. L.

Preparation of Thiazolines. By SIEGMUND GABRIEL and CARL VON HIRSCH (*Ber.*, 1896, **29**, 2609—2612).—Three methods already known are first recited. A better method than either of these, giving yields of 40—80 per cent. of the theoretical, is to heat a mixture of the hydrobromide of a bromalkylamine with a thiamide, rapidly to a suitable temperature (between 90° and 165°), and continue the heating until a portion of the mixture no longer gives any precipitate of a solid (thiamide) when water is added to it:



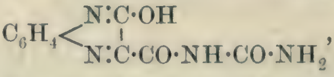
$$\begin{array}{l}CH_2Br\\ |\\ CH_2{\cdot}NH_2\end{array} + \begin{array}{l}HS\\ HN\end{array}\!\!>CR = \begin{array}{l}CH_2{\cdot}S\\ |\\ CH_2{:}N\end{array}\!\!>CR + NH_4Br.$$

In this manner, the following substances were prepared:—μ-Phenylthiazoline, from bromethylamine and thiobenzamide. β-Methyl-μ-phenylthiazoline, from β-bromopropylamine and thiobenzamide. *μ-Methylthiazoline*, from bromethylamine and thiacetamide, is an oil boiling at 144°. *μ-Ethylthiazoline*, from bromethylamine and thiacetamide, boils at 162°; the yellow *picrate* melts at 135°. *$\beta\mu$-dimethylthiazoline*, from β-bromopropylamine and thiacetamide, boils at 152°, and is oxidised by bromine water to β-methyltaurine. *$\beta\mu$-diethylthiazoline*, from β-bromopropylamine and thiopropionamide, boils at 172°.
C. F. B.

Quinoxaline Derivatives. By OSCAR HINSBERG (*Annalen*, 1896, **292**, 245—258.)—Quinoxaline *methiodide* crystallises in yellowish-red leaflets, and melts at 175°; the *ethiodide* separates from alcohol in red needles, and melts at 146°.

2′-Phenylquinoxaline, $C_6H_4{<}\begin{matrix}N{:}CH\\ |\\ N{:}CPh\end{matrix}$, is obtained by heating an alcoholic solution of bromacetophenone with orthophenylenediamine in molecular proportion; it crystallises in slender needles, and melts at 78°.

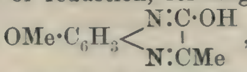
The *ureide* of 3′-hydroxyquinoxaline-2′-carboxylic acid,

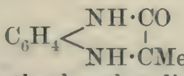


$$C_6H_4{<}\begin{matrix}N{:}C{\cdot}OH\\ |\\ N{:}C{\cdot}CO{\cdot}NH{\cdot}CO{\cdot}NH_2\end{matrix},$$

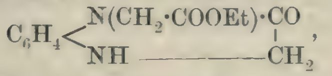
is obtained from alloxan and orthophenylenediamine; it crystallises in slender, yellow needles, and melts at 250°, becoming dark-coloured. By prolonged treatment with hot soda, it is converted into *3′-hydroxyquinoxaline-2′-carboxylic acid*, $C_6H_4{<}\begin{matrix}N{:}C{\cdot}OH\\ |\\ N{:}C{\cdot}COOH\end{matrix}$, which crystallises from alcohol in small, yellow needles, and melts at 265°, liberating carbonic anhydride; the *3′-hydroxyquinoxaline* thus formed sublimes in colourless needles which melt at 265°.

3′:2′-Hydroxymethylquinoxaline, $C_6H_4{<}\begin{matrix}N{:}C{\cdot}OH\\ |\\ N{:}CMe\end{matrix}$, is formed by the action of pyruvic acid on orthophenylenediamine; it melts at 245°.

Nitroparanisidine [$OMe:NO_2:NH_2 = 1:3:4$] is obtained by nitrating acetoparanisidide, and hydrolysing the product; it crystallises from alcohol in deep red needles, and melts at 129°. Pyruvic acid combines with the product of reduction, forming *3′-hydroxy-2*(or 3)*-methoxy-2′ methylquinoxaline*,  $OMe\cdot C_6H_3<\begin{array}{l}N{:}C\cdot OH\\ \quad | \\ N{:}CMe\end{array}$, which crystallises in small needles, and melts at 197°; the salts with mineral acids are yellow and the alkali derivatives colourless.

2-Dimethyl-3′-ketotetrahydroquinoxaline,  $C_6H_4<\begin{array}{l}NH\cdot CO\\ \quad\ | \\ NH\cdot CMe_2\end{array}$, is obtained from ethylic bromisobutyrate and orthophenylenediamine, and crystallises from alcohol in colourless needles, melting at 177°; the substance, which does not exhibit acidic properties, forms colourless salts with mineral acids.

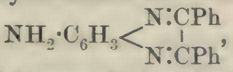
The *compound*, $C_{12}H_{14}N_2O_3$, which may have the constitution



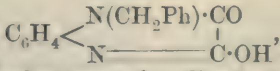
$$C_6H_4<\begin{array}{l}N(CH_2\cdot COOEt)\cdot CO\\ \qquad\qquad\qquad | \\ NH \text{———————} CH_2\end{array},$$

is derived from ethylic chloracetate and orthophenylenediamine, and crystallises in colourless prisms melting at 163°; alcoholic soda converts it into the *compound* $C_{10}H_{10}N_2O_3$, which crystallises from alcohol in needles, and melts at 212°. Sodium nitrite, in glacial acetic acid, converts the substance having the composition $C_{12}H_{14}N_2O_3$ into a compound which crystallises in colourless prisms, and melts at 155°, but does not exhibit the character of a nitroso-derivative; this compound and the original substance are oxidised by potassium dichromate and glacial acetic acid, giving rise to an acid which melts at 275°.

3-Nitroquinoxaline, $C_8N_2H_5\cdot NO_2$, is prepared by dissolving 4-nitro-orthophenylenediamine and the sodium hydrogen sulphite compound of glyoxal in water, in molecular proportion, and heating the mixture during several hours; it crystallises from dilute alcohol in long, brownish-yellow needles, and melts at 177°.

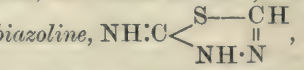
3 : 2′ : 3-*Nitrodiphenylquinoxaline* is obtained from benzil and 4-nitro-orthophenylenediamine, and forms colourless leaflets melting at 188°. Reduction with tin and hydrochloric acid converts it into *3 : 2′ : 3′-amidodiphenylquinoxaline*,  $NH_2\cdot C_6H_3<\begin{array}{l}N{:}CPh\\ \quad | \\ N{:}CPh\end{array}$, which is also produced when a solution of triamidobenzene hydrochloride and benzil in dilute alcohol is heated in a reflux apparatus; it crystallises from alcohol and melts at 175°, both the alcoholic and ethereal solutions exhibiting greenish-yellow fluorescence. The *hydrochloride* crystallises in deep red leaflets, and melts at 250°, and the *acetyl* compound crystallises from chloroform in silky leaflets, and melts at 252°.

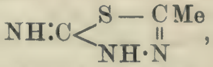
The *ureide* of 2(or 3)-amido-3′ : 2′-hydroxyquinoxalinecarboxylic acid, $NH_2\cdot C_8N_2H_3(OH)\cdot CO\cdot NH\cdot CO\cdot NH_2$, is obtained by heating a solution of 1 : 3 : 4-triamidobenzene with alloxan, and does not melt below 300°; the solutions in ethylic alcohol and acetic acid exhibit feeble, greenish yellow fluorescence. The action of hot ammonia converts it into the *acid*.

2′ : 3′-Hydroxyketo-1′-benzylquinoxaline,  $C_6H_4<\begin{array}{l}N(CH_2Ph)\cdot CO\\ \qquad\qquad\ | \\ N \text{————} C\cdot OH\end{array}$, is produced on fusing a mixture of benzylorthopenylenediamine and excess of oxalic acid at 160° ; it crystallises from glacial acetic acid, and melts at 265°. Phosphorus pentachloride at 160° gives rise to benzylic chloride and 2′:3′-dichloroquinoxaline.

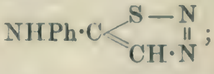
The author draws attention to certain regularities exhibited by the melting points of quinoxaline derivatives. M. O. F.

Derivatives of Thiobiazoline. By MARTIN FREUND and CARL MEINECKE (*Ber.*, 1896, **29**, 2511—2517. Compare Pulvermacher Abstr., 1894, i, 304 ; also Freund and Imgart, Abstr., 1895, i, 400).—*Formylthiosemicarbazide*, $NH_2 \cdot CS \cdot NH \cdot NH \cdot CHO$, crystallises from hot water or methylic alcohol in irregular plates, and melts at 174—175° ; it reduces cold Fehling's solution, and is devoid of basic properties. *Acetylthiosemicarbazide*, $NH_2 \cdot CS \cdot NH \cdot NHAc$, crystallises from water in colourless needles, and melts at 165° ; it reduces Fehling's solution.

5-*Imidothiobiazoline*,  $NH{:}C<\begin{matrix} S\text{—}CH \\ \quad \| \\ NH \cdot N \end{matrix}$, is obtained by the action of acetic chloride on formylthiosemicarbazide, and the *hydrochloride* crystallises from water in aggregates of needles melting at 149—150° ; the base crystallises from water in needles, and melts at 191°. The *nitroso*-derivative melts and decomposes at 220°, the *methiodide* at 243°, and the *acetyl* derivative at 268°.

5-*Methylimidothiobiazoline*,  $NH{:}C<\begin{matrix} S\text{—}CMe \\ \quad \| \\ NH \cdot N \end{matrix}$, is obtained by heating thiosemicarbazide with acetic chloride on the water bath, and crystallises from water in lustrous, white leaflets, melting at 235° ; the *hyrochloride* crystallises in white needles and melts at 110°, and the *nitroso*-derivative melts and decomposes at 227°. The *methiodide* melts at 215°, and the *methochloride* at 285° ; the *acetyl* derivative crystallises from water in white needles, and melts at 292°, whilst the sodium derivative of the latter crystallises in long, slender needles, and melts at 179°. M. O. F.

Action of Diazomethane on Phenylthiocarbimide. By HANS VON PECHMANN and AUGUST NOLD (*Ber.*, 1896, **29**, 2588—2593).—When an ethereal solution of diazomethane (prepared from 5 c.c. nitrosomethylurethane) is allowed to remain with 3·2 grams of phenylthiocarbimide, crystals are formed which melt and decompose at 172·5° (losing two-thirds of their nitrogen), evolve hydrogen sulphide when treated with acid reducing-agents, and are neutral in character. The substance is probably *anilidothiobiazole*, with the constitution



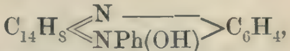
$$NHPh \cdot C<\begin{matrix} S\text{—}N \\ \quad \| \\ CH \cdot N \end{matrix} ;$$

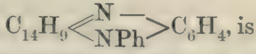
it is certainly different from Pulvermacher's anilidothiobiazoline (Abstr., 1894, i, 304). From its alcoholic solution, mercuric chloride precipitates a compound, $C_8H_6N_3SHgCl$, melting at 193° ; warm nitric acid converts it into an orange-yellow *trinitro*-derivative, which melts at 221°, and has acid properties ; its white *nitroso*-derivative melts at 98°, its *acetyl* and *benzoyl* derivatives at 162° and 157° respectively ; the last compound yields benzanilide when reduced with zinc dust and sulphuric acid. C. F. B.

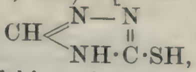
Hydrogenised Azines. By Oscar Hinsberg and H. Garfunkel (*Annalen*, 1896, **292**, 258—271).—As Claus has shown, ammonium sulphide converts phenazine into dihydrophenazine; this substance reduces ammoniacal silver, and the *diacetyl* derivative crystallises from alcohol in prisms, and melts at 180°. The green double salt of dihydrophenazine hydrochloride, described by Claus, has been obtained by the authors on reducing phenazine with stannous chloride and sodium amalgam.

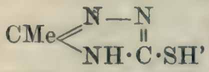
Naphthaphenazine *hydrochloride* crystallises from concentrated hydrochloric acid in small, brown prisms, and is decomposed by boiling water; it is indifferent towards alcoholic ammonium sulphide under ordinary conditions, but undergoes change when heated with this agent in sealed tubes at 160°. Reducing agents in acid solution convert it into a violet double salt, which is decomposed under the influence of boiling water.

Phenanthraphenazine *hydrochloride* crystallises from concentrated hydrochloric acid in small, brick-red needles, and is decomposed by hot water; acid reducing agents convert it into a violet double salt, which resembles the analogous compounds of dihydrophenazine and dihydronaphthaphenazine. The *acetyl* derivative of dihydrophenanthraphenazine crystallises in pale yellow leaflets, and melts at 252°; hot concentrated sulphuric and nitrous acids regenerate phenanthraphenazine.

Phenylphenanthraphenazonium hydroxide,  $C_{14}H_{8}{<}\begin{array}{l}N\text{————}\\ NPh(OH)\end{array}{>}C_6H_4$, is obtained in the form of acetate when orthamidodiphenylamine hydrochloride and phenanthraquinone are heated in glacial acetic acid with sodium acetate, and the liquid diluted with water. The *hydriodide* is sparingly soluble in water, and the *hydrochloride* crystallises in yellowish-brown prisms; the *hydrobromide* separates from water in yellowish-brown crystals.

n-Phenyldihydrophenanthraphenazine,  $C_{14}H_{9}{<}\begin{array}{l}N\text{——}\\ NPh\end{array}{>}C_6H_4$, is obtained by reducing the foregoing base with stannous chloride, and crystallises from chloroform in colourless leaflets, melting at 230°; the *hydrochloride* is colourless, and sparingly soluble in water, the solution in glacial acetic acid developing with ferric chloride a bluish violet coloration. M. O. F.

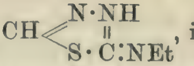
Preparation of Triazole and its Homologues. By Martin Freund (*Ber.*, 1896, **29**, 2483—2490. Compare Pulvermacher, Abstr., 1894, i, 304).—[With Carl Meinecke.]—*Triazole-thiol* (*mercaptotriazole*),  $CH{<}\begin{array}{l}N-N\\ \qquad\ \ \|\\ NH\cdot C\cdot SH\end{array}$, is obtained by heating moderate quantities of formylthiosemicarbazide at 190°, the operation being interrupted when evolution of ammonia and sulphurous acid takes place; it is readily soluble in water and alcohol, insoluble in ether, benzene, and chloroform, and crystallises in slender needles, melting at 215—216°. The aqueous solution, which has an acid reaction, yields precipitates with many metallic salts dissolved in water; hot, concentrated sulphuric acid liberates sulphurous anhydride. The *bisulphide*, $C_4H_4N_6S_2$, is produced under the influence of a 3 per cent. solution of hydrogen peroxide; it crystallises from glacial acetic acid in prisms, and melts at 222°. On gently heating a solution of mercaptotriazole containing hydrogen peroxide, the bisulphide which is first formed is converted into triazole (compare Abstr., 1892, 735).

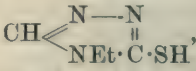
2-*Methyltriazole-5-thiol* (*mercapto-c-methyltriazole*,  $\mathrm{CMe}{<}\begin{array}{l}\mathrm{N{-}N}\\ \mathrm{NH{\cdot}C{\cdot}SH}\end{array}$, is formed when acetylthiosemicarbazide is heated at 185°; it crystallises from water in white needles, and melts at 260—261°.

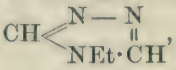
[With HEINRICH P. SCHWARZ.]—*Ethylthiosemicarbazide*,

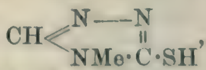
$$NHEt{\cdot}CS{\cdot}NH{\cdot}NH_2,$$

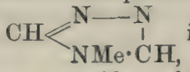
is obtained from hydrazine hydrate and ethylthiocarbimide in alcoholic solution; it crystallises from alcohol, and melts at 84°. *Formylethylthiosemicarbazide*, $NHEt{\cdot}CS{\cdot}NH{\cdot}NH{\cdot}CHO$, is derived from the foregoing derivative by the action of formic acid, and crystallises in lustrous leaflets, melting at 163—164°; it is feebly acidic in character.

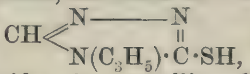
5-*Ethylimidothiobiazoline*,  $\mathrm{CH}{<}\begin{array}{l}\mathrm{N{\cdot}NH}\\ \mathrm{S{\cdot}C{:}NEt}\end{array}$, is obtained by the action of acetic chloride on finely-powdered formylethylthiosemicarbazide, the *hydrochloride*, which crystallises in rhombs and melts at 212°, being deposited by the solvent on evaporation; the base, which is hygroscopic, is sparingly soluble in ether, but dissolves readily in alcohol and water.

1-*Ethyltriazole-5-thiol* (*n-ethylmercaptotriazole*),  $\mathrm{CH}{<}\begin{array}{l}\mathrm{N{-}N}\\ \mathrm{NEt{\cdot}C{\cdot}SH}\end{array}$, is produced when formylethylthiosemicarbazide is heated at 180—190° for 10—15 minutes; it crystallises from dilute alcohol in slender needles, and melts at 96—97°. The *sodium* derivative decomposes at 145°, and the *silver* derivative melts above 300°; copper and platinum salts also give rise to metallic derivatives.

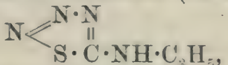
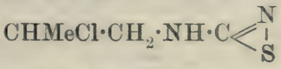
1-*Ethyltriazole*,  $\mathrm{CH}{<}\begin{array}{l}\mathrm{N{-}N}\\ \mathrm{NEt{\cdot}CH}\end{array}$, obtained from 1-ethylmercaptotriazole and 3 per cent. hydrogen peroxide, is a viscous, yellowish oil, which dissolves in water; the *hydrochloride*, which separates in rhombic crystals on adding ether to the alcoholic solution, melts at 196°.

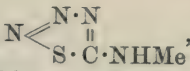
1-*Methyltriazole-5-thiol* (*n-methylmercaptotriazole*),  $\mathrm{CH}{<}\begin{array}{l}\mathrm{N{-}N}\\ \mathrm{NMe{\cdot}C{\cdot}SH}\end{array}$, is produced on heating formylmethylthiosemicarbazide (Pulvermacher, *loc. cit.*) above its melting point, and separates from water in crystals, which melt at 168°; it crystallises unchanged from hydrochloric acid, but the solution in soda deposits the *sodium* derivative, which sinters at 130°, and decomposes at 200°. The *platinochloride* is crystalline, and the *silver* derivative amorphous.

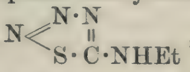
1-*Methyltriazole*,  $\mathrm{CH}<\begin{array}{l}\mathrm{N—N}\\ \quad\;\, |\\ \mathrm{NMe\cdot CH}\end{array}$, is obtained from 1-methylmercaptotriazole and hydrogen peroxide, and readily absorbs water and carbonic anhydride; it melts at 90°, and the aqueous solution is alkaline. The *platinochloride* crystallises in prisms, and the *mercurichloride* crystallises from hot water in plates, and melts at 175°.

1-*Allyltriazole*-5-*thiol*,  $\mathrm{CH}<\begin{array}{l}\mathrm{N———N}\\ \qquad\quad \|\\ \mathrm{N(C_3H_5)\cdot C\cdot SH}\end{array}$, is obtained by heating formylallylthiosemicarbazide; it crystallises from water, and melts at 111°.

M. O. F.

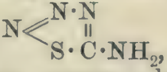
Derivatives of Triazosulphole [Thiotriazole.] By MARTIN FREUND and HEINRICH P. SCHWARZ (*Ber.*, 1896, **29**, 2491—2499).—*Allylamidothiotriazole*,  $\mathrm{N}<\begin{array}{l}\mathrm{N\cdot N}\\ \;\;\; \|\\ \mathrm{S\cdot C\cdot NH\cdot C_3H_5}\end{array}$, is obtained by the action of nitrous acid on allylthiosemicarbazide, and crystallises in yellowish leaflets on adding petroleum to the alcoholic solution; it melts at 54°, and has basic properties. Hot water quickly liberates sulphur and nitrogen, with production of allylcyanamide. Dilute sulphuric acid also liberates sulphur and nitrogen; whilst hot, concentrated hydrochloric acid sets free one-half the available nitrogen, forming the *compound*,  $\mathrm{CHMeCl\cdot CH_2\cdot NH\cdot C}<\begin{array}{l}\mathrm{N}\\ |\\ \mathrm{S}\end{array}$; this substance is a syrup, and its *platinochloride* crystallises in anhydrous octahedra, and melts at 235°. Caustic soda causes a complete decomposition of allylamidothiotriazole, giving rise to sulphur, hydrogen sulphide and azoimide.

Methylamidothiotriazole,  $\mathrm{N}<\begin{array}{l}\mathrm{N\cdot N}\\ \;\;\; \|\\ \mathrm{S\cdot C\cdot NHMe}\end{array}$, is produced by the action of nitrous acid on methylthiosemicarbazide, and melts at 96° when crystallised from ether; hot water converts it into trimethylisomelamine, obtained by von Hofmann from methylcyanamide. When the solution of methylamidothiotriazole in concentrated hydrochloric acid is gently heated, nitrogen is eliminated without liberation of sulphur; the concentrated liquid deposits methylthiocyanamide hydrochloride.

Ethylamidothiotriazole,  $\mathrm{N}<\begin{array}{l}\mathrm{N\cdot N}\\ \;\;\; \|\\ \mathrm{S\cdot C\cdot NHEt}\end{array}$, crystallises from ether and melts at 66—67°; boiling water converts it into triethylisomelamine.

M. O. F.

Amidotriazosulphole [Amidothiotriazole.] By MARTIN FREUND and ALFRED SCHANDER (*Ber.*, 1896, **29**, 2500—2505).—It having been shown that nitrous acid converts phenylthiosemicarbazide into a tetrazole derivative (Abstr., 1895, i, 193), it became of interest to ascertain whether thiosemicarbazide undergoes a similar change. Thiosemicarbazide can be obtained from hydrazine sulphate by an improved method, in quantity amounting to 70 per cent. of the theoretical; the *hydrochloride* crystallises from hydrochloric acid in slender needles, and melts at 186 to 190°, according to the rate at which the temperature is raised.

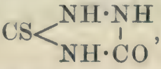
Amidothiotriazole,  $\mathrm{N}<\begin{matrix}\mathrm{N{\cdot}N}\\ \quad\| \\ \mathrm{S{\cdot}C{\cdot}NH_2}\end{matrix}$, is obtained by cautiously adding sodium nitrite to an aqueous solution of thiosemicarbazide hydrochloride; it crystallises from ether in long, transparent needles, and melts at 128—130° with slight explosion. It dissolves in alcohol, glacial acetic acid, ethylic acetate, ethylic acetoacetate and aniline, without undergoing decomposition, and is sparingly soluble in chloroform and carbon bisulphide; it is insoluble in benzene, toluene, and xylene. Aqueous silver nitrate causes decomposition and liberation of gas; ammoniacal silver nitrate produces a white precipitate which rapidly decomposes, even when protected from light. Boiling water liberates nitrogen and sulphur, with production of cyanamide, whilst aniline, under the same conditions, converts amidothiotriazole into dicyandiamide; concentrated hydrochloric acid first forms the *hydrochloride* which decomposes at 96°, and when heated gives rise to the hydrochloride of thiocyanamide. Bromine converts it into the hydrobromide of thiocyanamide, and alkalis liberate sulphur and azoimide.

M. O. F.

Thiourazole. By MARTIN FREUND and ALFRED SCHANDER. (*Ber.*, 1896, **29**, 2506—2511). *Hydrazothiodicarbonamide*,

$$NH_2{\cdot}CS{\cdot}NH{\cdot}NH{\cdot}CO{\cdot}NH_2,$$

is obtained from thiosemicarbazide hydrochloride and potassium, cyanate; it sinters at 210°, and melts and decomposes at 218—220°.

Thiourazole,  $\mathrm{CS}<\begin{matrix}\mathrm{NH{\cdot}NH}\\ \quad| \\ \mathrm{NH{\cdot}CO}\end{matrix}$, is obtained by heating a solution of the foregoing substance in concentrated hydrochloric acid for half an hour in a reflux apparatus, and filtering off the thiosemicarbazide hydrochloride which separates on cooling; it crystallises from hot water, and melts at 177°. The substance is both basic and acidic, and is indifferent towards ferric chloride and hydrogen peroxide.

When hydrazothiodicarbonamide is oxidised with ferric chloride, it yields a *hydrochloride*, $C_4H_8N_8SO_2$,HCl, which crystallises from water, and melts at 219—224°; the *base* crystallises from hot water, and melts at 204—205°. Fusion converts hydrazothiodicarbonamide into a white, crystalline compound, which sinters at 220°, and melts at 235—240°.

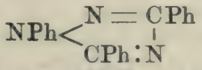
Phenylhydrazothiodicarbonamide, $NH_2{\cdot}CS{\cdot}NH{\cdot}NH{\cdot}CO{\cdot}NHPh$, is obtained from thiosemicarbazide and phenylic cyanate; it sinters at 210°, and melts at 217—218°. Concentrated hydrochloric acid converts it into diphenylcarbamide, semicarbazide hydrochloride, and thiourazole.

M. O. F.

Action of Hydrazines on Nitriles under the Influence of Sodium. By R. ENGELHARDT. (*J. pr. Chem.*, 1896, [2], **54**, 143—

176).—To prepare the compound obtained by Walther (*Abstr.*, 1894, i, 503) from the action of phenylhydrazine (1 mol.) on benzonitrile (2 mols.) in the presence of sodium, the hydrazine and nitrile are dissolved in benzene, and sodium is added until it no longer dissolves; the mixture is then heated in a reflux apparatus to complete the reaction, much ammonia being evolved during the process. A little alcohol is now added to dissolve the remaining sodium, the benzene is distilled off, and the residue crystallised from hot alcohol. A very small proportion of sodium is necessary, so that the formation of a definite sodium derivative does not seem to be essential for the change; nor is sodium cyanide formed to any extent. The yield is 90 per cent. of the mixed hydrazine and nitrile.

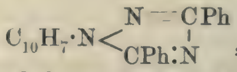
Analyses of the compound agree with the formula $C_{20}H_{15}N_3$ (compare *loc. cit.*), which is confirmed by cryoscopic determinations of the molecular weight. The stability of the compound indicates a closed ring structure, and, after discussing various possibilities, the author concludes that the reaction consists in the formation of a hydrazidine from the phenylhydrazine and benzonitrile, which then forms, with another molecule of benzonitrile, a phenyldibenzenylhydrazidine (compare Pinner, Abstr., 1894, i, 385); by loss of ammonia this would yield the new compound, which may, therefore, be regarded as a triphenyltriazole (*loc. cit.*).

1:3:5-*Triphenyltriazole*,  $\mathrm{NPh}{<}\begin{array}{l}\mathrm{N=CPh}\\ \qquad\;|\\ \mathrm{CPh{:}N}\end{array}$, crystallises in colourless prisms, melts at 104°, boils above 360°, and is soluble in most solvents, except water. Ordinary oxidising and reducing agents are without action on the compound. The *hydrochloride*, $C_{20}H_{15}N_3,HCl$, melts and decomposes at 169°; it is insoluble in cold water and is decomposed by warm water into the base and hydrogen chloride. The nitro-derivatives are under examination. The *ethiodide*, $C_{20}H_{15}N_3,EtI$, melts at 145°; by dissolving it in dilute sulphuric acid and adding sodium hydroxide, a precipitate is obtained which, when dissolved in hydrochloric acid and treated with platinic chloride, yields the *platinochloride* of the *ethochloride* $(C_{20}H_{15}N_3)_2,Et_2PtCl_6$. The *methohydroxide* crystallises in white granules (with benzene of crystallisation), melts at 181°, and is soluble in alcohol but not in ether or water. The *platinochloride* of the *methochloride* was also prepared.

1:3:5-*Phenyldiorthotolyltriazole* is prepared by substituting orthotolunitrile for benzonitrile in the above prescription; it crystallises in white, felted needles, melts at 86°, and is very soluble in the usual solvents, except water. 1:3:5-*Phenyldiparatolyltriazole* is similarly prepared; it crystallises in nacreous laminæ, melts at 115°, and dissolves in the usual solvents, except water; the *hydrochloride* melts at 180°.

3:5:1-*Di-α-naphthylphenyltriazole* was prepared from phenylhydrazine and α-naphthonitrile, but could not be crystallised or otherwise purified. 3:5:1-*Di-β-naphthylphenyltriazole* crystallises in flocculent aggregates of white needles, melts at 160°, and dissolves easily in hot pyridine, amylic alcohol, chloroform, glacial acetic acid, benzene, acetone and ethylic acetate; more sparingly in ethylic and methylic alcohols, ether and light petroleum, but not in water.

Attempts to produce Pinner's diphenyltriazole (*loc. cit.*) by the action of hydrazine sulphate on benzonitrile in presence of sodium proved abortive.



1 : 3 : 5-*β-Naphthyldiphenyltriazole,* $C_{10}H_7\cdot N<\begin{array}{l}N{-}CPh\\ \qquad\ \ |\\ CPh{:}N\end{array}$, was prepared from β-naphthylhydrazine and benzonitrile by this method; it crystallises in white needles, melts at 144° and dissolves freely in benzene, ether, glacial acetic acid and hot alcohol, more sparingly in light petroleum, and not at all in water. No triazoles could be formed from acetonitrile or propionitrile and phenylhydrazine under the influence of sodium.

When a secondary, unsymmetrical hydrazine is caused to react with a nitrile in the manner under consideration, the two compounds condense in molecular proportion to form a hydrazidine. *Phenylbenzenylmethylhydrazidine,* $NMePh\cdot NH\cdot CPh{:}NH$, is prepared from benzonitrile (1 mol.) and β-methylphenylhydrazine (1 mol.) by dissolving the compounds in benzene and treating the solution with sodium; the operations are similar to those described at the beginning of this abstract. The hydrazidine is crystallised by dissolving it in benzene and adding light petroleum until the solution becomes turbid; after a time, long, yellow crystals separate, which become pale yellow needles on repeating the process; they melt at 105°, and exhibit basic properties. *Phenylbenzenylethylhydrazidine* resembles the methyl-derivative in every respect, and also melts at 105°, its *platinochloride* melts at 196°.

Diphenylbenzenylhydrazidine, $NPh_2\cdot NH\cdot CPh{:}NH$, from β-diphenylhydrazine and benzonitrile, crystallises in slender, pale yellow needles, melts at 170°, and is only sparingly soluble in cold alcohol, ether and benzene, but is insoluble in light petroleum and water; the *hydrochloride,* $C_{19}H_{17}N_3,HCl$, is described. The *acetyl*-derivative,

$$NPh_2\cdot N\cdot N{:}CPh\cdot NHAc,$$

crystallises in intensely yellow needles, and melts at 185°; this is the sole acetyl-derivative which could be obtained. The *nitroso*-derivative, $NPh_2\cdot N(NO)\cdot CPh{:}NH$, crystallises in yellow needles, and melts at 206°.

No reaction occurs between nitriles and symmetrical hydrazines under the influence of sodium. A. G. B.

Creatinines of Different Origin. By M. TOPPELIUS and HERBERT POMMEREHNE (*Arch. Pharm.*, 1896, **234**, 380—397).—Johnson (Abstr., 1889, 165) has described several creatinines, but the authors find them to be identical. They prepared a creatinine from urine; they converted this by prolonged boiling with water into creatine, and the creatine back into creatinine by evaporation with hydrochloric acid; they prepared creatinine from the creatine of meat extract; and, lastly, from creatine obtained synthetically from cyanamide and methylamidoacetic acid. The hydrochlorides of all these creatinines crystallised anhydrous from fairly strong hydrochloric acid, but with H_2O from water; in 2 per cent. solution at 15°, all gave an angle of of refraction of 64° 45′ in the Pulfrich refractometer, and all were inactive to polarised light. The base itself in all cases dissolved in about 10·7 parts of water at 15° and about 625 parts of absolute alcohol at 17°, and had the same reducing action on Fehling's solution. The aurochlorides in all cases melted at about 162° and reacted in the same way with ether. The platinochloride in all cases melted at about 210°, and dissolved in about 36 parts of water at 13°. The picrate in all cases melted at about 213°. C. F. B.

Action of Methylic Iodide on Xanthine Salts (Pseudotheobromine). By HERBERT POMMEREHNE (*Arch. Pharm.*, 1896, **234**, 367—380).—There are three possible dimethylxanthines, $C_7H_8N_4O_2$. Of these, one is the naturally occurring theobromine, prepared also artificially by E. Fischer by acting on the lead derivative of xanthine with methylic iodide. The second, theophylline, occurs in tea-leaves, and has been prepared by E. Fischer from dimethyluric acid. What is probably the third isomeride is obtained, together with small quantities of, apparently, theobromine and theophylline, when the silver derivative of xanthine is heated with methylic iodide at 130—140°. The theobromine separates as the alcoholic extract is concentrated; the theophylline is precipitated with mercuric nitrate, and finally the new substance is precipitated by means of silver nitrate; to it the name of *pseudotheobromine* is given. It is a white substance which crystallises imperfectly and does not melt below 280°; when its solution is mixed with chlorine water, evaporated, and the residue treated with ammonia, a red coloration is produced. Its *hydrobromide*, *hydrochloride*, *platinochloride*, and *aurochloride* strictly resemble those of theobromine, except that the two first retain their halogen acid at 100°, instead of losing it, as the analogous salts of theobromine do. A small quantity of pseudotheobromine was obtained on one occasion when methylic iodide was boiled with a solution of xanthine in alcoholic potash; theobromine itself is, however, the main product, and on another occasion was the only one. C. F. B.

Action of Wagner's Reagent on Caffeine and a New Method for the Estimation of Caffeine. By MOSES GOMBERG (*J. Amer. Chem. Soc.*, 1896, **18**, 331—342).—The author draws attention to the fact that, although an aqueous solution of caffeine gives no precipitate with Wagner's reagent (a solution of iodine in potassium iodide), yet an acidified solution readily gives a precipitate of caffeine periodide, $C_8H_{10}N_4O_2,HI,I_4$. This periodide is not identical with the one obtained by Tilden (this Journal, 1865, **18**, 99). When dry it forms a violet-blue amorphous powder, melting at 213°; when moist, it rapidly loses iodine on exposure to the air, but it is permanent when dry and suffers only slight loss when heated at 100°. It also loses but little iodine when suspended in water; it readily dissolves in alcohol, especially on heating, and a considerable portion is decomposed into the free base and iodine. Its methyl alcoholic solution, on spontaneous evaporation, leaves the periodide in the form of beautiful six-sided prisms, with a metallic dark-bluish lustre. It is insoluble in carbon bisulphide, but dissolves in hot ethylic acetate without undergoing decomposition.

The author has used Wagner's reagent for the estimation of caffeine, but the method is only applicable when other substances, which might be precipitated by the iodine, are absent. Definite volumes of acidified (best with hydrochloric acid) solutions of caffeine are precipitated with a known volume of iodine in potassium iodide; after complete precipitation, an aliquot part of the supernatant liquid is obtained, either by filtration or decantation, and the excess of iodine in it titrated by decinormal sodium thiosulphate. In the calculation, 1 part of iodine $= 0{\cdot}3834$ parts of caffeine, or 1 c.c. of $N/10$ iodine $= 0{\cdot}00485$ gram of caffeine. The results obtained by this method are very exact, the best being obtained when the iodine is in large excess. The author also recommends the method for the estimation of caffeine in drugs containing it. J. J. S.

Caffeine Perhaloids. By MOSES GOMBERG (*J. Amer. Chem. Soc.*, 1896, **18**, 347—377).—Caffeine hydriodide di-iodide, $C_8H_{10}N_4O_2,HI,I_2$, is obtained when a solution of caffeine in dilute alcohol, containing some hydriodic acid, is exposed to sunlight in a warm place. The diiodide is only formed when the deposition of crystals is rapid, if the liberation of iodine is slow, the tetriodide is formed. It melts at 171°. The crystals, according to the author, are anhydrous, whereas Tilden (this Journal, 1865, **18**, 99) gives the composition as $(C_8H_{10}N_4O_2,HI,I_2)_2 + 3H_2O$.

Caffeine hydriodide tetriodide, $C_8H_{10}N_4O_2,HI,I_4$, is obtained by treating an acidified solution of caffeine with Wagner's reagent (compare preceding abstract). It is the most stable periodide of caffeine, and is the one usually obtained. It may also be obtained by passing hydrogen iodide into a chloroform solution of caffeine and iodine, or by triturating caffeine hydrobromide dibromide or tetrabromide with an aqueous solution of potassium iodide.

Caffeine hydrobromide tetriodide, $C_8H_{10}N_4O_2,HBr,I_4$, is readily obtained when a slow stream of hydrogen bromide is passed into a chloroform solution of caffeine and iodine. It is never formed in the presence of hydrogen iodide. It is usually amorphous, but can be crystallised, has a dark brown chocolate colour, and melts at 183°.

Caffeine hydrochloride di-iodide, $C_8H_{10}N_4O_2,HCl,I_2$, is obtained by passing hydrogen chloride into a chloroform solution of caffeine and iodine. It forms small, crystalline granules of a pale brown colour, and melts at 165°.

Caffeine hydrobromide tetrabromide, $C_8H_{10}N_4O_2,HBr,Br_4$. Whenever bromine is allowed to act on caffeine, this perbromide is one of the first products formed. It is produced in presence or in absence of hydrogen bromide, in presence of water, of chloroform, or when pure bromine is employed. It crystallises in small, orange-red, prismatic crystals, and melts sharply at 170°, but is previously converted into the dibromide. On exposure to the air, it loses 2 atoms of bromine, yielding the corresponding *dibromide*, which is more stable. The author controverts the statements of Maly and Hinteregger (Abstr., 1882, 629), and also of E. Fischer (*Annalen*, **215**, 264), that on the addition of pure bromine to caffeine a dibromide, $C_8H_{10}N_4O_2,Br_2$, is formed. The only products are the tetrabromide already mentioned and the corresponding derivative of monobromocaffeine.

Caffeine hydrobromide dibromide, $C_8H_{10}N_4O_2,HBr,Br_2$, obtained by exposing the tetrabromide to the air or by treating it with ether, is an amorphous, yellow powder, and melts at 170°.

Caffeine hydrochloride tetrabromide is somewhat difficult to prepare. The bromine must be perfectly free from hydrogen bromide, and must be used in dilute solution only, moreover the chloroform must be free from alcohol and moisture. It has a lighter colour than the corresponding hydrobromide, and melts at 149°.

Chlorocaffeine hydriodide, $C_8H_9ClN_4O_2,HI$, can only be obtained in the absence of water. It forms white, heavy crystals, and is readily decomposed by water and by alcohol. The corresponding *hydrobromide* is even less stable, and the *hydrochloride* the least stable.

Chlorocaffeine hydriodide pentiodide, $C_8H_9ClN_4O_2,HI,I_5$, is a black, amorphous powder with a slightly bluish tint, and melts at 185—186°. The corresponding *hydrobromide*, $C_8H_9ClN_4O_2,HBr,I_5$, is not so black as the hydriodide, melts at 169°, and is very unstable.

Chlorocaffeine hydrochloride tetriodide, $C_8H_9ClN_4O_2,HCl,I_4$, is bluish-black, and melts at 137°.

Chlorocaffeine hydrobromide pentabromide, $C_8H_9ClN_4O_2,HBr,Br_5$, obtained by treating a chloroform solution of chlorocaffeine with bromine, crystallises in dark red, short, thick prisms, and melts at 151°. On digesting with ether for several days, it is converted into *chlorocaffeine hydrobromide monobromide*, $C_8H_9ClN_4O_2,HBr,Br$, which is a yellow, amorphous powder, and melts at 189°.

Chlorocaffeine hydrochloride pentabromide. $C_8H_9ClN_4O_2,HCl,Br_5$, forms small, scarlet-red prisms, and melts at 153°.

Bromocaffeine hydriodide, *hydrobromide*, and *hydrochloride* have been prepared, and are all fairly stable.

Bromocaffeine hydriodide pentiodide forms a dull black, amorphous powder, and melts at 183°.

Bromocaffeine hydrobromide pentiodide is a dark brown, amorphous powder, which melts at 160°.

Bromocaffeine hydrochloride tetriodide is very unstable; it consists of brown or dark blue crystals, and melts at 136°.

Bromocaffeine hydrobromide pentabromide, obtained in a similar manner to the corresponding derivative of chlorocaffeine, forms dark orange-red prisms, and melts at 156°.

Bromocaffeine hydrobromide monobromide, obtained from the pentabromide by treatment with anhydrous ether, is a light yellow powder, which melts and decomposes at 206°.

Bromocaffeine hydrochloride pentabromide is readily decomposed, and melts at 157°.

These compounds are, as a rule, decomposed by water and other solvents, by exposure to moist air, or by heating at 100°. Details are given in the original. J. J. S.

Action of Methylic Iodide on Papaveric Acid. By GUIDO GOLDSCHMIEDT and ALFRED KIRPAL (*Monatsh.*, 1896, 17, 491—505).—The substance melting at 122—124°, obtained by Schranzhofer (Abstr., 1894, i, 59), may be prepared by heating the monomethylic salt of papaveric acid (compare Abstr., 1893, i, 180), with methylic alcohol and a little sulphuric acid, and is therefore the dimethylic salt of papaveric acid, $C_6H_3(OMe)_2{\cdot}CO{\cdot}C_5NH_2(COOMe)_2$; when heated with hydrochloric acid, it yields papaveric acid, and not the methylbetaïne as was supposed by Schranzhofer; the same result is obtained if alkali be employed.

Schranzhofer's second substance (m. p. = 195—197°, *loc. cit.*) is found on examination to contain three methoxyl-groups and is readily prepared by the etherification of papaveric acid; it is therefore a monomethylic salt of that acid, $C_6H_3(OMe)_2{\cdot}CO{\cdot}C_5NH_2(COOMe){\cdot}COOH$, and is doubtless the γ-alkyl salt, that prepared by the etherification of papaveric anhydride being therefore the β-derivative. Attempts to prepare *methylic pyropapaverate* from the foregoing γ-methylic papaverate were unsuccessful; it may, however, be made by heating pyropapaveric acid with methylic alcohol and sulphuric acid; it crystallises from methylic alcohol in beautiful, long, white, silky needles, and melts at 108°.

Analyses of the substance melting at 192—194° (Schranzhofer, *loc. cit.*), made with a view of determining the number of methyl groups attached to oxygen and nitrogen respectively, show that its molecule is more complicated than was supposed by its discoverer, and may be written $C_{28}H_{12}N_2MeO_9(OMe)_5$. Constitutional formulæ for the substance are suggested, and the paper concludes with analyses of the platinochloride $(C_{34}H_{30}N_2O_{14})_2,H_2PtCl_6 + 8H_2O$, which confirm the above formula. A. L.

Optical Rotation of Atropine and its Salts. By J. Gadamer (*Arch. Pharm.*, 1896, **234**, 543—551).—The author has succeeded in preparing pure atropine by treating *Atropin. purissimum Merck* with moderately concentrated alcoholic soda for several months. After recrystallisation and repeated conversion into the sulphate and reconversion into the free base, perfectly pure atropine is obtained. In this form, it is optically inactive, and its salts are also quite devoid of optical activity. Atropine prepared in this way melts at 115·5—116°, the anhydrous sulphate melts at 180—181°, and the hydrated salt ($1H_2O$) at 161°, or 151—154°, according to the rate at which it is heated. The oxalate melts at 188—188·5° and is anhydrous; Hesse gives the melting point as 176°. Hyoscyamine oxalate melts at 173° (176° Hesse). The author has obtained the *aurochloride* of a new alkaloid from crude duboisine, but this has not yet been completely analysed; it melts at 198° and forms characteristic spherical aggregates. A. H.

Scopolamine and i-Scopolamine. By Oswald Hesse (*Ber.*, 1896, **29**, 2439—2442. Compare Abstr., 1896, i, 655).—The author maintains, in opposition to E. Schmidt (Abstr., 1896, i, 712), that the so-called ordinary scopolamine hydrobromide is simply a mixture of the hydrobromides of hyoscine and atroscine. A. H.

Organic Chemistry.

Theory of the Pyrogenic Reactions of Aliphatic Hydrocarbons. By Fritz Haber (*Ber.*, 1896, **29**, 2691—2700).—Berthelot's theory, with its assumption of a limiting equilibrium, and Lewes' theory of the luminosity of flame, are criticised, and, in part, rejected. These investigators obtained abnormal results because they experimented with paraffins containing only one or two atoms of carbon in the molecule. The author has experimented with hexane, and also with trimethylethylene, acetylene, and benzene. To avoid secondary reactions, the gas was exposed for a few seconds only to the high temperature; this was attained by passing it in a current through a heated tube. At a temperature of 600—800°, neither carbon nor an appreciable quantity of hydrogen was liberated; what happens is a shifting of a hydrogen atom, with formation of an olefine and either methane or ethane, the latter, if formed at all, being always formed in smaller amount. Thus hexane yields amylene and methane. Trimethylethylene also yields methane, but it yields ethylene in addition, although this requires a complete change in the arrangement of the atoms of carbon. Long ago, too, Thorpe and Young (*Annalen*, 1873, **165**, 1) noticed that the distillation of paraffin yields no hydrogen, but lower hydrocarbons; in this case, however, of approximately equal molecular weight. In the case of the paraffins, then, the union between carbon and carbon is more easily dissolved than that between carbon and hydrogen. The opposite is the case with aromatic hydrocarbons; benzene, for instance, yields diphenyl and hydrogen. It decomposes, however, much less easily than hexane. In addition to the products mentioned above, hexane yields a little benzene; this, however, is obtained equally from trimethylethylene, and is doubtless formed by a secondary reaction from the acetylene first produced.

At 900—1000°, the reaction is quite different; coke, tar, and hydrogen are formed, and methane is the only paraffin to be found, ethylene the only olefine; ethylene and hydrogen therefore do not unite to form ethane at this temperature. Acetylene (at 800°) yields but a little ethylene with much hydrogen; a great part of the gas is unchanged. Methane alone is entirely stable.

Incidentally, it is shown how the results of a gas analysis, including an explosion of the residual gas after absorption, may be utilised to infer the presence or absence in the gas of ring compounds with the composition $C_n H_{2n}$, such as trimethylene. The results of such analyses lead one to assume the presence of such hydrocarbons in coal-gas.

C. F. B.

Limiting the Explosive Proportions of Acetylene, and Detecting and Measuring the Gas in Air. By Frank Clowes. (*Chem. News*, 1896, **74**, 188. See this vol. ii, 128.)

Decomposition of Sugars under the Influence of Acids. By Marcellin Berthelot and Gustave André (*Compt. rend.*, 1896, **123**, 567—580).—The authors have investigated more especially the formation of carbonic anhydride, humic, levulinic, and formic acids by the action of dilute mineral acids on various sugars. Phosphoric acid was preferred to hydrochloric or sulphuric acid, because it does not volatilise with steam and exerts no oxidising action on the sugars. Some of the experiments were made at 100°, in sealed tubes from which the air had been removed; others in flasks at the ordinary pressure, sometimes with a reflux condenser, sometimes with an ordinary condenser so that the volatile products were removed as fast as they were formed. The substances estimated, as a rule, were glucose, carbonic anhydride, carbonic oxide, formic acid, humic acid, which was dried and weighed at 100°, levulinic acid, which was estimated by the method of coefficients of distribution between water and ether (*Ann. Chim. Phys.*, 1872, [4], **26**, 396 and 433), furfuraldehyde, and water.

Glucose, when heated in sealed tubes at 100° with about five times its weight of phosphoric acid and six times its weight of water, yields carbonic anhydride and carbonic oxide in small quantity, and formic, levulinic, and humic acids. Even after 115 hours, 12 per cent. of the glucose remains unchanged, and the phenomena indicate that a large part, at least, of the glucose is first changed into glucosan, which then undergoes decomposition. The quantity of formic acid is higher than corresponds with the quantity of levulinic acid, but part of it is formed at the same time as the humic acid. Direct experiments show that there is a considerable and variable difference between the rates of formation of the levulinic and humic acids. The carbonic oxide results mainly from secondary decomposition of the formic acid, but part of it is formed by the action of the acid on the glucose. Direct experiments show that the levulinic acid yields neither carbonic oxide nor humic acid. The greater part of the carbonic anhydride is produced in the earlier stages of the decomposition, and results chiefly from the direct action of the acid on the glucose, although a small quantity is formed by the prolonged action of acids on levulinic acid.

In flasks at the ordinary pressure, there is an increase in the proportion of carbonic anhydride, and this is not due to oxidation, since the same result is obtained in an atmosphere of hydrogen; furfuraldehyde is also formed. As in the experiments with tubes, there is no fixed relation between the formic acid and humic acid; there also seems to be evidence of the formation of a small quantity of acetic acid. The proportion of volatile acids formed seems to be greatest when sulphuric acid is used, but the proportion of humic acid shows no similar variation. The higher proportion of carbonic anhydride formed during distillation cannot be attributed to decomposition of levulinic acid.

The isomerides of glucose, galactose, levulose, and maltose behave in a similar way, and when distilled with acids yield a notable proportion of carbonic anhydride, and also a small quantity of furfuraldehyde. As Tollens and Grote have observed, the production of humic acid from levulose is more rapid than in the case of the other sugars, but all the other changes are also more rapid with levulose than with the others.

The more concentrated the acids, the greater is the proportion of humic acid formed. The complicated nature of the reaction is a natural result of the complicated constitution of the glucoses; the production of formic acid, for example, may be attributed to the splitting off of the last aldehydic molecule of the generatrix of the glucose. C. H. B.

Arabinose. By MARCELLIN BERTHELOT and GUSTAVE ANDRÉ (*Compt. rend.*, 1896, **123**, 625—631).—The authors have studied the action of water and acids on arabinose and on furfuraldehyde under various experimental conditions. No furfuraldehyde was formed when dilute aqueous solution of arabinose was distilled at 100°, but when heated with water for 5 hours at 200°, almost one-half of the theoretical yield of furfuraldehyde was obtained. Three experiments are described in which arabinose was heated in sealed tubes with (1) saturated aqueous hydrochloric acid, (2) 25 times its weight of 12·3 per cent. hydrochloric acid, and (3) dilute aqueous phosphoric acid. Of the products formed, namely, carbonic anhydride, carbonic oxide, formic acid, furfuraldehyde, organic acids, and humic matters, about 92 per cent. of the carbon of the arabinose taken appeared as humic matter, and in no case was more than a trace of furfuraldehyde obtained, the latter being decomposed and polymerised under the conditions of experiment. Gum arabic, when heated in a sealed tube at 100° with concentrated aqueous hydrochloric acid, gave similar results, but with more dilute hydrochloric acid a larger proportion of carbonic anhydride was formed. When arabinose (5 grams) was slowly distilled with dilute aqueous phosphoric acid, for 590 hours, the evaporated water being replaced from time to time, it yielded 0·2999 gram of carbonic anhydride, and 1·9632 gram of furfuraldehyde. It is remarked in conclusion that when arabinose is submitted to the action of dilute acids, three classes of reactions occur simultaneously. (1) The formation of furfuraldehyde, which marks a distinction between the pentoses and hexoses. (2) The formation of humic acid, more especially in sealed tubes. (3) The formation of carbonic anhydride, more marked under conditions of slow distillation, a decomposition common to the pentoses and the hexoses. A. C. C.

Isoallylamine (1-Aminopropylene). By SIEGMUND GABRIEL and CARL VON HIRSCH (*Ber.*, 1896, **29**, 2747—2751).—The authors have succeeded in preparing this base, which had previously only been obtained in aqueous solution, by distilling β-propylamine hydrobromide with 33 per cent. aqueous potash, and fractionating the distillate. Isoallylamine, $CHMe\colon CH\cdot NH_2$ is a colourless, mobile liquid, which fumes in the air, has the characteristic odour of the amines, is very hygroscopic, and is miscible with water; it boils at 66—67° (751 mm. pressure), has a sp. gr. 0·812 at 16°, and burns with a luminous flame. The base readily undergoes change when its solution in water is heated. In addition to the salt with bismuth iodide, which has been previously described, it was only possible to obtain the *platinochloride*, which is an orange red, crystalline powder. It acts as a poison, and exerts a remarkable specific action on the so-called papillary part of the kidneys, in this respect resembling vinylamine. It reacts in the normal manner with chloroform and potash, and with nitrous acid, but does not undergo the thiocarbimide reaction. With carbon bisulphide, it forms ββ-methyl-μ-mercaptothiazoline (Hirsch, Abstr., 1890, 859); this substance melts at 95—97°, and not at 82° as stated by Hirsch. The base readily unites with the halogen acids, forming the corresponding substituted propylamine. *β-Chloropropylamine picrate* melts at 158°. *β-Iodopropylamine hydriodide* is a crystalline powder. The *picrate* melts at 150°. Sulphurous acid converts the base into β-methyltaurine, $C_3H_9NO_3S$.

The base is accompanied by a *polymeride*, $(C_3H_7N)_2$, which boils at 143—145°, and has the normal vapour density corresponding with the above formula. A. H.

Action of Sodium on Acetaldehyde. By Paul C. Freer (*Annalen*, 1896, **293**, 326—338. Compare Abstr., 1894, i, 65).—The production of sodium acetone, $CH_2{:}CMe{\cdot}ONa$, by the action of metallic sodium on a dilute xylene solution of acetone (*loc. cit.*), suggested the possibility of obtaining the sodium derivative of vinylic alcohol, $CH_2{:}CH{\cdot}ONa$, by treating acetaldehyde with the metal. Acetaldehyde is vigorously attacked by sodium, hydrogen being liberated and a crystalline substance formed, but, owing to the unstable character of this product, it is necessary to study the action in presence of benzoic chloride, which gives rise to a solid benzoyl derivative of an aldehydo-aldol.

Aldehydo aldol benzoate, $OBz{\cdot}CHMe{\cdot}CH_2{\cdot}CH{<}^{O}_{O}{>}CHMe$, is prepared by heating ether, acetaldehyde, and benzoic chloride with metallic sodium in a reflux apparatus, from which air is excluded by means of a current of hydrogen; after 24 hours, the ethereal liquid is treated successively with water and dilute potash, being finally dried with calcium chloride, and allowed to evaporate. The substance crystallises from petroleum in colourless, transparent prisms, and melts at 86—87°; when heated with water in sealed tubes at 100°, benzoic acid, aldol, and acetaldehyde are produced, whilst distillation gives rise to benzoic acid, crotonaldehyde, and acetaldehyde. Although insoluble in cold, dilute caustic potash, it dissolves on heating the liquid, which then becomes yellow owing to the production of aldehyde-resin; the substance is indifferent towards bromine, phenylhydrazine, and cold, aqueous potassium permanganate.

The production of a benzoate by the action of sodium on acetaldehyde in presence of benzoic chloride may be explained in two ways—either aldehyde, under the influence of sodium, is condensed to aldol, the sodium derivative of which is then produced, and combines with benzoic chloride, or the sodium derivative of acetaldehyde is first produced, undergoing condensation with more aldehyde to form the sodium derivative of aldehydo-aldol, which yields the benzoate in presence of benzoic chloride. The latter explanation is the more probable, owing to the fact that the action of sodium on aldol gives rise to a derivative which is not identical with the initial product of the action of the metal on acetaldehyde.

As the syrup from which aldehydo-aldol benzoate separates in the first instance undergoes decomposition when kept, depositing benzoic acid, it must be examined without delay. A solution of bromide in chloroform acts on it immediately, without liberating hydrogen bromide, and benzoic acid is formed, along with an oily substance containing bromine; phenylhydrazine gives rise to benzophenylhydrazide, and a resinous phenylhydrazone; the readiness with which hydrolysis takes place suggesting the presence of an oxygen ether (compare Nef, Abstr., 1893, i, 629), which is probably aldol benzoate. This view is confirmed by the fact that the original syrup, when distilled, yields benzoic and crotonic acids, acetaldehyde, crotonaldehyde, and a small quantity of isocrotonaldehyde; moreover, when sodium acts on aldol in presence of benzoic chloride, hydrogen is liberated, and the oily product is identical with the syrup which remains after separating aldehydo-aldol benzoate. M. O. F.

Action of Aqueous Potassium Hydroxide and Carbonate on Isobutaldehyde. By MAXIMILIAN BRAUCHBAR (*Monatsh.*, 1896, 17, 637—647. Compare Fossek, Abstr., 1882, 1279, and especially Franke, Abstr., 1896, i, 404.)—When isobutaldehyde is allowed to remain for 2 weeks in a closed vessel at the ordinary temperature, in contact with an equal volume of aqueous potassium hydroxide (containing 92 grams KOH per litre), it is largely converted into di-isobutaldehyde, some isobutyric acid being also formed. If the mixture is allowed to remain for 5 weeks, the main product is Fossek's "di-isopropylglycol," melting at 52°, but some di-isobutaldehyde is still obtained; the glycol is formed from the di-isobutaldehyde, a part of which is reduced to the glycol at the expense of another part, which becomes oxidised to isobutyric acid. Di-isobutaldehyde may be obtained unmixed with other substances, and in much better yield, by using potassium carbonate instead of the hydroxide; isobutaldehyde is allowed to remain for six weeks in contact with an equal volume of a saturated solution of the carbonate.

Di-isobutaldehyde is obtained as a liquid, but it crystallises when kept, and then melts at 90—92°. At 218°, its vapour is completely dissociated into that of isobutaldehyde; as a consequence of this easy dissociation, it is largely decomposed when distilled, even under diminished pressure; it boils between 90° and 120° under a pressure of about 16 mm. It yields a *monacetyl derivative* as a pale yellowish oil boiling at 136—139° under 18 mm. pressure; also a *monoxime* as a colourless, viscid oil boiling at 140° under 16 mm. pressure. It is reduced by sodium amalgam and dilute sulphuric acid to di-isopropyl glycol $CHMe_2\cdot CH(OH)\cdot CMe_2\cdot CH_2\cdot OH$, and oxidation with permanganate converts it into Fossek's acid,

$$C_8H_{16}O_3[=CHMe_2\cdot CH(OH)\cdot CMe_2\cdot COOH],$$

melting at 92°, together with some di-isopropyl ketone. These reactions of di-isobutaldehyde lead to the adoption of the formula

$$CHMe_2\cdot CH(OH)\cdot CMe_2\cdot CHO$$

for it; it is formed from isobutaldehyde by an aldol condensation.

C. F. B.

Action of Alcoholic Soda on Isobutaldehyde. By ADOLF FRANKE (*Monatsh.*, 1896, 17, 672—676).—Contrary to Urbain's statement (Abstr , 1896, i, 590), isobutaldehyde, when heated with 5 per cent. alcoholic soda without cooling, yields a glycol,

$$CHMe_2\cdot CH(OH)\cdot CMe_2\cdot CH_2\cdot OH,$$

but not one of the three products he enumerates. At $-20°$, the product is di-isobutaldehyde (compare Brauchbar, preceding abstract); the oxime of this substance, when heated with acetic anhydride for 9 hours at 120°, yields the *acetyl* derivative of a *nitrile*,

$$CHMe_2\cdot CH(OAc)\cdot CMe_2\cdot CN,$$

as an oil which boils at 112° under 16 mm. pressure, and yields the acid, $CHMe_2\cdot CH(OH)\cdot CMe_2\cdot COOH$, when hydrolysed with aqueous potash.

C. F. B.

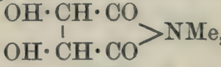
Hydrazidoacetic Acid. By Wilhelm Traube and E. Hoffa (*Ber.*, 1896, **29**, 2729—2730).—Isonitraminacetic acid, on reduction with sodium amalgam at 0° in slightly acid solution, yields hydrazidoacetic acid; this cannot be separated in the ordinary way by extraction with benzaldehyde, but on employing salicylaldehyde in its place, the condensation product readily separates as a white, crystalline precipitate. This orthohydroxybenzylidenehydrazido-acetic acid is, when pure, a colourless compound, becoming, however, brown when exposed to the air; it is readily soluble in alcohol and ether. It exists in two stereoisomeric forms, melting at 78° and 105° respectively. On removal of salicylaldehyde, free *hydrazidoacetic acid* is produced, forming colourless crystals, melting at 145°. It is very soluble in water, scarcely soluble in alcohol and ether. The *hydroiodide*, $NH_2\cdot NH\cdot CH_2\cdot COOH,HI$, melts at 156°. J. F. T.

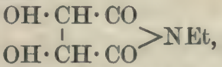
Electrolysis of Potassium Xanthate in Aqueous Solution. By J. F. Carl Schall (*Chem. Centr.*, 1896, i, 588; from *Zeits. Elektrotechn. u. Elektrochemie*, 2, 475—476.)—By the electrolysis of potassium xanthate in concentrated aqueous solution, *ethylic bis-dithiocarbonate*, $S_2(CS\cdot OEt)_2$, is formed by the union of the anions $EtO\cdot CSS$. It separates at first as a yellow oil, which subsequently solidifies to a crystalline mass. The process is analogous to the formation of acetyl and benzoyl bisulphides by the electrolysis of the potassium salts of thioacetic and thiobenzoic acids respectively, as observed by Bunge (*Ber.*, 1870, 3, 297). E. W. W.

Methylenecarbamide. By Bernhard Tollens (*Ber.*, 1896, **29**, 2751—2752).—Goldschmidt, in a recent paper on the action of formaldehyde on carbamide (this vol., i, 22) has omitted to refer to the papers of Hölzer (*Ber.*, **17**, 659; **18**, 3302), and Lüdy (Abstr., 1889, 1059), on the same subject. A. H.

Asymmetric Nitrogen, V. Imides of Tartaric Acid and of Benzoyltartaric Acid. By Albert Ladenburg (*Ber.*, 1896, **29**, 2710—2719).—Further facts are brought forward in support of the theory of the asymmetric nitrogen atom. The two benzylmalimides of Giustiniani can either be structural- or stereo-isomerides. The former supposition seems improbable, from the fact that such isomerism has never as yet been observed in the case of inactive acids. Preparations of the imides of dibasic acids, such as succinic acid, inactive malic acid, meso-tartaric acid, and racemic acid showed that they existed in one form only. The occurrence of two isomeric benzylmalimides is, then, a further instance in support of the theory of the asymmetric nitrogen atom, and can be explained in the same way as in the case of isoconiine. Other substituted malimides are in the course of investigation.

Substituted imides of tartaric acid are best prepared by heating the bitartrate of a primary amine above its melting point.

Tartarmethylimide,  $\begin{matrix}\text{OH}\cdot\text{CH}\cdot\text{CO}\\ | \\ \text{OH}\cdot\text{CH}\cdot\text{CO}\end{matrix}>\text{NMe}$, from the bitartrate of methylamine (m.p. 170°), crystallises from alcohol in colourless, rhombic needles, melts at 178°, and has a rotation $[\alpha]_D = 193{\cdot}69°$. A second substance of the same composition is obtained on evaporating the mother liquor; this melts at 152°—153°, but was subsequently found to be a mixture of the methylimides of *d*- and *r*-tartaric acid, and not an homogeneous substance.

Tartarethylimide,  $\begin{matrix}\text{OH}\cdot\text{CH}\cdot\text{CO}\\ | \\ \text{OH}\cdot\text{CH}\cdot\text{CO}\end{matrix}>\text{NEt}$, prepared in the same way as the methylimide, melts at 171—174°, and has a rotation of $[\alpha]_D =$ 165—166°.

The corresponding derivatives of benzoyltartaric acid are prepared by the action of benzoic chloride on the tartarimide. By the action of benzoic chloride on tartarmethylimide, only a very small quantity of the mono-benzoyl compound is produced, the chief product being *dibenzoyltartarmethylimide*, which crystalllies from alcohol in colourless prisms containing alcohol of crystallisation, and having the formula $4C_{19}H_{15}NO_6,3C_2H_6O$; it melts at 68°. On heating, the alcohol is rapidly given off, and two isomeric compounds are formed, the proportions of which depend on the temperature of decomposition. On heating at 100° for 1—2 hours, *a-dibenzoyltartarmethylimide* is produced, melting at 56°, and this, at the ordinary temperature, passes slowly into the β-compound.

β-Dibenzoyltartarmethylimide is best formed by heating the compound containing alcohol of crystallisation at 60° for 6—10 hours; it melts at 106°—107°, and at that temperature passes into the α-compound. The optical rotation for the α-component is 183·9, and for the β- 188·8, the difference being only very slight. It is, therefore, highly probable that these compounds are stereo-isomerides, and their occurrence can only be explained by the assumption of an asymmetric nitrogen atom.

The author concludes with a brief summary of his ideas as to the nature and function of the asymmetric nitrogen atom. He no longer supposes that it is possible to obtain optically active nitrogen compounds containing no asymmetric carbon atom, but understands by an asymmetric nitrogen atom, an atom serving to modify the activity produced by the asymmetric carbon atom, as is seen in the cases of isoconiine, the benzylmalimides and the dibenzoyltartarmethylimides. He further defines an asymmetric nitrogen atom as such that two of its valencies must form a ring compound, whilst the third is otherwise combined. Such a ring must, however, possess neither symmetry nor pseudo-symmetry, and must, therefore, be optically active. The capability of the third nitrogen bond to take up two, and perhaps in many rings four positions of equilibrium, causes stereoisomerism.

J. F. T.

Imides of Racemic Acid. By HERMANN WENDE (*Ber.*, 1896, **29**, 2719—2721).—The imides of racemic acid are prepared by heating the biracemate of the corresponding alkylamine above its melting point. The *methylimide* from *methylamine biracemate* (m. p. 180°) melts at 157—158°, and crystallises from alcohol in lustrous needles. *Ethylamine biracemate* melts at 142—143°, and, on heating, passes into the *ethylamide*, melting at 179°. The *propylamine* salt melts at 147°, and the *propylimide* crystallises in glistening needles. *Aniline biracemate* separates when molecular quantities of racemic acid and aniline are mixed; the crystals contain 1 mol. H_2O and melt and decompose at 173°; the *phenylimide* melts at 235—236°. Benzylamine biracemate melts at 178°. The *benzylimide* formed from this crystallises from glacial acetic acid in leaflets melting at 168°. J. F. T.

Ethereal Phosphopalladates and their Ammoniacal Derivatives. By E. FINCK (*Compt. rend.*, 1896, **123**, 603—604).—*Ethylic phosphopalladate*, $P_2(OEt)_6PdCl_2$, forms red, prismatic crystals, insoluble in water, but soluble in alcohol. It is obtained by placing phosphopalladic chloride and absolute alcohol in separate dishes under a bell jar, which also encloses a dish containing quick lime. *Methylic phosphopalladate* is strictly analogous to it in composition and is obtained in a similar way; it crystallises in white, prismatic needles, soluble in alcohol, benzene, and ether.

When treated with ammonia in presence of water or benzene, ethylic phosphopalladite yields colourless crystals of the composition

$$P(OEt)_3PdCl_2,2NH_3,$$

whilst in presence of alcohol the product is $P(OEt)_3PdN_2H_4,2HCl +$ $P(OEt)_3NH_3PdN_2H_4,2HCl$. The methyl derivative yields analogous compounds under the same conditions.

Ethylic phosphopalladate, when evaporated with aqueous ammonia, yields white, deliquescent crystals of the compound

$$P_2O(OEt)_5PdNH_2,HCl,$$

whilst the methyl derivative yields the compound

$$P_2(OMe)_6N_2H_4,2HCl\ [?\ P_2(OMe)_6PdN_2H_4,2HCl].$$

When heated with paratoluidine and alcohol, ethylic phosphopalladite yields white, prismatic crystals of the compound $P(EtO)_3C_7H_9N,PdCl_2$; an analogous methyl derivative is obtained in the same way. Pyridine, under similar conditions, yields the compounds

$$P(OEt)_3C_5NH_5,PdCl_2 \text{ and } P(OMe)_3C_5NH_5,PdCl_2.$$

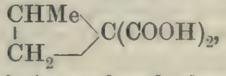
C. H. B.

Constitution of Vinaconic [Trimethylenedicarboxylic] Acid. By RICHARD MARBURG (*Annalen*, 1896, **294**, 89—134. Compare Abstr., 1895, i, 171).—The main facts which lead the author to support the view of W. H. Perkin, jun., who regards vinaconic acid as trimethylenedicarboxylic acid, have been already described (*loc. cit.*); the present paper contains an amplified record of the experimental details.

Ethylic γ-chlorisosuccinate, $CH_2Cl{\cdot}CH_2{\cdot}CMe(COOEt)_2$, obtained from ethylic sodioisosuccinate and ethylenic chloride, boils at 127—128° under a pressure of 9 mm.; not more than 10 per cent. of this salt is produced, and a certain amount of ethylic symmetrical α-dimethyladipindicarboxylate [hexane-2 : 2 : 4 : 4-tetracarboxylate] is also formed (compare Abstr., 1894, i, 441.) When ethylic γ-chlorisosuccinate is heated at 260—270°, it yields ethylic α-methylbutyrolactonecarboxylate (compare Abstr., 1895, i, 171). The *barium* salt of α-methylbutyrolactonecarboxylic acid contains $4H_2O$, the *calcium* salt, $1H_2O$, whilst the *silver* salt is anhydrous. *Barium* hydroxyethylisosuccinate contains $3H_2O$, and the *silver* salt crystallises from water.

α-Methylbutyrolactone is obtained on heating the lactonecarboxylic acid at 140°, carbonic anhydride being eliminated; this substance is also produced on hydrolysing γ-phenoxyethyl-α-methylacetic acid (Trans., 1896, 173). The *barium, calcium,* and *silver* salts of α-methyl-γ-hydroxybutyric acid are anhydrous.

Methylvinaconic (1-*methyltrimethylene*-2 : 2-*dicarboxylic*) *acid,*



the ethylic salt of which is produced when ethylic sodiomalonate is treated with propylenic bromide (Abstr., 1895, i, 172), crystallises from benzene in lustrous needles, and melts at 113·5°; the *barium* salt contains $2H_2O$, the *hydrogen barium* salt $3H_2O$, and the *calcium* salt $5H_2O$, whilst the *silver* and *hydrogen silver* salts are anhydrous, and crystallise from water. Methylvinaconic acid is quite distinct from allylmalonic acid.

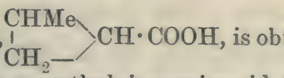
γ-*Bromopropylmalonic acid,* $CHMeBr{\cdot}CH_2{\cdot}CH(COOH)_2$, is obtained by the action of hydrobromic acid on methylvinaconic acid, and when crystallised from chloroform, melts at 107·5°; it is identical with the acid produced on treating allylmalonic acid with the same agent, and boiling water converts it into the γ-methyl-α-butyrolactonecarboxylic (valerolactonecarboxylic) acid, obtained by Hjelt from the hydrogen bromide additive compound of allylmalonic acid.

The *bromine additive compound* of methylvinaconic acid,

$$C_4H_6Br_2(COOH)_2,$$

crystallises from chloroform in needles, and melts and decomposes at 130—131°; the bromine additive compound of allylmalonic acid melts at 124·5°. Methylvinaconic acid is very readily attacked by concentrated nitric acid, and after 10—20 hours two molecular proportions of carbonic anhydride are eliminated; vinaconic acid, on the other hand, yields no gas during the first 5 days, the quantity eliminated after 20 days representing less than a tenth part of one molecular proportion.

1 : 2-*Methyltrimethylenecarboxylic acid,*



is obtained along with valerolactone on submitting methylvinaconic acid to dry distillation above 140°; it is a colourless, limpid liquid, having the odour of butyric acid, and boils at 190—191° under a pressure of 745 mm. It remains liquid at – 18°, and has the sp. gr. = 1·030 at 0°/4° and 1·015 at 18°/4°. The *calcium* salt contains $1\frac{1}{2}H_2O$, the *barium* salt $2H_2O$; the *silver* salt is also crystalline. Methyltrimethylenecarboxylic acid is distinct from ethylidenepropionic and allylacetic acids.

M. O. F.

Mesitylene from Acetone. By VICTOR MEYER and W. MOLZ (*Ber.*, 1896, **29**, 2831—2833). (Compare Abstr., 1896, i, 547.)—The fractions of mesitylene of high-boiling point prepared from acetone do not yield any appreciable quantity of monoketones when treated with acetic chloride and aluminium chloride; it is improbable, therefore, that they contain hemimellithene. The observation made by Lucas and Sohn that a small quantity of hemimellithenecarboxylic acid is produced by the carboxylation of mesitylene, is doubtless to be explained by the occurrence of isomeric change similar to that which obtains when symmetrical durene is treated in the same way.

A. L.

Constitution of the Nitroso-derivatives of the Two Secondary Ethylidenanilines. By ALEXANDER EIBNER (*Ber.*, 1896, **29**, 2977—2981).—The two isomeric ethylidenanilines described by von Miller and Plöchl (Abstr., 1894, i, 410) both yield nitroso-derivatives, which are sulphur-yellow powders, soluble in hot alcohol and in benzenes; on the addition of ether to these solutions, the compounds are obtained in bright yellow, glistening crystals. The nitroso-compound from the base obtained by Eckstein melts at 161°, and is sparingly soluble in hot alcohol, but insoluble in ether; that from the author's base melts at 120°, is readily soluble in hot alcohol and only sparingly so in ether.

Both compounds, when reduced with tin and hydrochloric acid, yield the same products, namely, tetrahydroquinaldine and paraphenylenediamine. This reaction agrees with the formula

$$NO{\cdot}NPh{\cdot}CHMe{\cdot}CH_2{\cdot}CH{:}N{\cdot}C_6H_4{\cdot}NO \quad [N:NO = 1:4]$$

for the two nitroso-compounds.

On adding ferric chloride to a solution of the hydrochlorides of tetrahydroquinaldine and paraphenylenediamene in molecular proportion, a beautiful green coloration is produced, which turns to blue on the addition of water.

Other secondary Schiff's bases can yield similar nitroso-compounds—for example, Sender's propylidenaniline (Abstr., 1892, 1189) and the base from orthotoluidine and acetaldehyde.

J. J. S.

Orthophenylenebiguanide. By RUDOLF ZIEGELBAUER (*Monatsh.*, 1896, **17**, 648—666).—Monamines, NH_2R or NHR_2, simply combine with dicyanodiamide, $C_2H_4N_4$, yielding substituted biguanides, $C_2H_6RN_5$ or $C_2H_5R_2N_5$. Orthophenylenediamine hydrochloride, however, when it is heated with dicyanodiamide, in molecular proportion, in alcoholic solution for 7 hours at 105°, reacts with evolution of ammonia. The product formed, however, has still the properties of a biguanide, and the constitution $C_6H_4{<}\begin{matrix}NH{\cdot}C(NH)\\NH{\cdot}C(NH)\end{matrix}{>}NH$ must be assigned to it. The author concludes that this and other reactions of dicyanodiamide are best explained by adopting the formula $CN{\cdot}NH{\cdot}C(NH){\cdot}NH_2$ for that substance.

Orthophenylenebiguanide, $C_8H_9N_5,H_2O$, crystallises in yellowish, nacreous plates, and melts and decomposes at 242° (uncorr.). The following salts were prepared: *nitrate*, $(C_8H_9N_5)_3,5HNO_3 + 3H_2O$ ($\frac{9}{10}$ths of the nitric acid can be titrated with baryta); *hydrochloride*, $C_8H_9N_5,HCl$; *platinochloride*, $C_8H_9N_5,PtCl_4 + 2H_2O$, orange-yellow, darkens above

260°, but is still unmelted at 300°; *sulphates*, $C_8H_9N_5,H_2SO_4 + 4H_2O$ and $(C_8H_9N_5)_2,H_2SO_4 + H_2O$, the latter brownish in colour; *chromate*, $C_8H_9N_5,H_2Cr_2O_4$, yellow; *ferrocyanide* $(C_8H_9N_5)_2,H_4FeC_6N_6 + 3H_2O)$, yellowish. A red *cobalt* and a chocolate-brown *nickel* derivative, $(C_8H_8N_5)_3Co + 3\frac{1}{2}H_2O$ and $(C_8H_8N_5)_2Ni$, were also prepared; such metallic derivatives are obtained by mixing a solution of a salt of the biguanide with a salt of the metal in question, pouring the mixture into a large quantity of hot, dilute alkali hydroxide, and allowing the whole to cool. C. F. B.

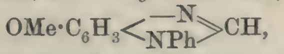
Reduction Products from Azo-compounds. By PAUL JACOBSON, M. JAENICKE and FRIEDRICH MEYER (*Ber.*, 1896, **29**, 2680—2690). —The reduction of benzene azoanisoïl, $OMe\cdot C_6H_4\cdot N_2Ph$, and benzeneazoveratrole, $C_6H_4(OMe)_2\cdot N_2Ph$ [$(OMe)_2 = 3:4$], have been studied, only ethylic ethers having been previously examined. The reduction and subsequent operations were carried out just as in the case of benzeneazophenetoïl (Abstr., 1896, i, 23). Benzeneazoanisoïl behaves like the last substance, yielding the ortho- and para-semidine bases,

$$OMe\cdot C_6H_3(NH_2)\cdot NHPh\ [OMe:NH_2:NHPh = 1:4:3]$$
$$\text{and } OMe\cdot C_6H_4\cdot NH\cdot C_6H_4\cdot NH_2,$$

in addition to the bases anisidine and aniline, which result from a division of the molecule; the quantitative relations are also similar. Benzeneazoveratrole also undergoes a similar reduction, but the action could not be studied quantitatively, for the main reaction is accompanied by another, which results in the removal of one methoxyl group, and the formation of a benzidine base,

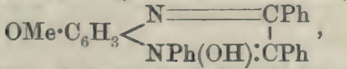
$$NH_2\cdot C_6H_3(OMe)\cdot C_6H_4\cdot NH_2.$$

2-*Amido-5-methoxydiphenylamine* (orthosemidine base) melts at 73°, and yields a *carbon bisulphide* derivative, $C_{14}H_{12}N_2SO$, melting at 208°; a yellow *salicylidene* derivative, $C_{20}H_{18}N_2O_2$, melting at 132° and oxidised by mercuric oxide to a *salicylic* derivative, $C_{20}H_{16}N_2O_2$, melting at 123°; with formic acid, a *methenyl* derivative,



$$OMe\cdot C_6H_3 \Big< \begin{matrix} -N- \\ NPh \end{matrix} \Big> CH,$$

melting at 77°; and with benzil, a *stilbazonium base*,



$$OMe\cdot C_6H_3 \Big< \begin{matrix} N{=\!=\!=\!=}CPh \\ \quad\quad\quad | \\ NPh(OH):CPh \end{matrix},$$

melting at 163—165°. 4-*Amido-4'-methoxydiphenylamine* (parasemidine base) melts at 102°.

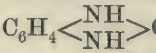
Benzeneazoveratrole was prepared from crystallised guaiacol by diazotising the latter, and boiling the sodium salt of the product, benzeneazoguaiacol, with alcoholic methylic iodide; it is red, and melts at 44·5—45°. 2-*Amido*-4:5-*dimethoxydiphenylamine* (orthosemidine base) has a pale violet colour, and melts at 151°; its *methenyl derivative* melts at 106—107°. 4:4'-*Diamido-2-methoxydiphenyl* (benzidine base), is pale pink, and melts at 104°. Incidentally, the *acetyl* derivative of amidoveratrole, $C_6H_3(OMe)_2\cdot NHAc$, was prepared; it is silver-grey, and melts at 132·5—133°.

Guaiacoldis-azobenzene, $OMe\cdot C_6H_2(OH)(N_2Ph)_2$, is obtained at the same time as benzene-azoveratrole; it is dark grey with a violet sheen, and melts at 150—155°. *Benzeneazoguaiacol*, obtained as mentioned above, forms red prisms, melting at 70·5—71·5° C. F. B.

Uramides, Urethanes, and Oxamethanes of Paraphenylenediamine and Metaphenylenediamine. By Hugo Schiff and Adriano Ostrogovich

(*Annalen*, 1896, **293**, 371—388. Compare Abstr., 1894, i, 236, 333).—The derivatives of paraphenylenediamine have been already described (*loc. cit.*), and the paper contains a tabular representation of their relationship; a description of the metaphenylenediamine derivatives appears for the first time.

Acetylmetaphenylenediamine *hydrochloride*, $HCl,NH_2\cdot C_6H_4\cdot NHAc$, is obtained by heating metaphenylenediamine dihydrochloride and sodium acetate in molecular proportion with water; it forms a reddish, crystalline mass, having no definite melting point, and softens at 194°.

Metacetamidophenylcarbamide, $NHAc\cdot C_6H_4\cdot NH\cdot CONH_2$, is produced on mixing cold, concentrated, aqueous solutions of acetylmetaphenylenediamine hydrochloride and potassium cyanate; it crystallises in reddish needles, and melts at 225°. Metaphenylenecarbamide,  $C_6H_4{<}\substack{NH\\NH}{>}CO$, is also produced in small quantity, and the same substance is obtained when acetamidophenylcarbamide is submitted to frequent recrystallisation.

Metamidophenylcarbamide hydrochloride, $HCl,NH_2\cdot C_6H_4\cdot NH\cdot CO\cdot NH_2$, is formed when a very concentrated solution of acetamidophenylcarbamide is boiled with hydrochloric acid for 10 minutes; it crystallises from dilute alcohol in lustrous scales, and melts at 281—282°

Metamidophenyloxamic acid, $NH_2\cdot C_6H_4\cdot NH\cdot CO\cdot COOH$, has been already described by Klusemann (this Journal, 1875, 269) and melts at 225°; the *hydrochloride* crystallises in needles and decomposes above 300°, whilst the *potassium* salt crystallises in yellow scales, and decomposes about 270°. The *acetyl* derivative melts at 125°, and begins to decompose at 130°. *Uramidophenyloxamic acid*,

$$NH_2\cdot CO\cdot NH\cdot C_6H_4\cdot NH\cdot CO\cdot COOH,$$

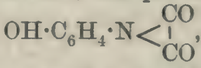
is obtained by heating potassium amidophenyloxamate with carbamide at 130°, and also from amidophenyloxamic acid and potassium cyanate; it crystallises from water in small needles, and melts at 230°.

Metaphenylenedioxamic acid, $C_6H_4(NH\cdot CO\cdot COOH)_2$, is obtained by heating alcoholic acetylmetaphenylenediamine with ethylic oxalate in a reflux apparatus; it separates from alcohol in crystalline aggregates, and melts, decomposing, at 240°. M. O. F.

βγ-Substituted Derivatives of Hydantoin. By Enrico Quenda

(*Chem. Centr.*, 1896, i, 701; from *Ann. Chim. Farm.*, **23**, 61—64). —Methylglycocine and monoparatolylcarbamide, when heated at 135—140°, yield diparatolylcarbamide and *γ-paratolyl-β-methylhydantoin*, the former being insoluble in water. The latter, which gives Weyl's reaction, melts at 112—113°, is soluble in water, and easily so in alcohol. Similarly, monorthotolylcarbamide and methyl-glycocine form diorthotolylcarbamide, which melts at 250°, and *γ-orthotolyl-β-methylhydantoin*. The latter, which was neither obtained in a crystalline form, nor analysed, does not give Weyl's reaction. E. W. W.

Derivatives of Paramidophenol. By VICTOR WIRTHS (*Arch. Pharm.*, 1896, **234**, 620—634.)—The entry of a dibasic acid radicle into the amido-group of an amidophenol may be effected by heating the latter with an acid anhydride or amide in an oil-bath or over a free flame. Phthalylparamidophenol has already been obtained by this method (Piutti, Abstr., 1886, 1026).

Succinylparamidophenol, $OH\cdot C_6H_4\cdot N⁚(CO)_2⁚C_2H_4$, from succinic anhydride and paramidophenol, crystallises in needles, melts at 270°, and is insoluble in all the usual solvents, except alcohol and glacial acetic acid. *Oxalylparamidophenol*,  $OH\cdot C_6H_4\cdot N{<}\begin{matrix}CO\\ |\\ CO\end{matrix}$, may be prepared by heating either oxalic acid or oxamide with paramidophenol; it crystallises in needles, does not melt at 350°, and sublimes when sharply heated, being at the same time partly decomposed.

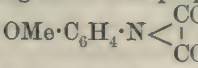
The derivatives under consideration can also be prepared by heating paramidophenol with ethereal salts in a sealed tube at 160°. The foregoing oxalyl derivative has been obtained in this way. With diethylic tartrate, 2 molecules of amidophenol enter into the reaction, yielding *tartronyldiparamidophenol*,

$$OH\cdot C_6H_4\cdot NH\cdot CO\cdot CH(OH)\cdot CH(OH)\cdot CO\cdot NH\cdot C_6H_4\cdot OH,$$

which crystallises in reddish needles, melts and decomposes at 282°, and dissolves in glacial acetic acid and alcohol.

Succinylparanisidine, $OMe\cdot C_6H_4\cdot N⁚(CO)_2⁚C_2H_4$, prepared by melting succinic anhydride with anisidine, crystallises in needles, melts at 162°, and dissolves in hot water and alcohol. Succinylparaphenetidine melts at 158° (Piutti, *Chem. Zeit.*, 1896, **20**, 54). *Succinyldiparaphenetidine*, $OEt\cdot C_6H_4\cdot NH\cdot CO\cdot C_2H_4\cdot CO\cdot NH\cdot C_6H_4\cdot OEt$, crystallises in needles, melts at 258°, and is insoluble in water.

By heating anisidine or phenetidine with ethereal salts in tubes at 150—160°, the following have been prepared.

Oxalylparanisidine,  $OMe\cdot C_6H_4\cdot N{<}\begin{matrix}CO\\ |\\ CO\end{matrix}$, which crystallises in needles, melts at 115°, and dissolves in water and alcohol. *Oxalyldiparanisidine*, $C_2O_2(NH\cdot C_6H_4\cdot OMe)_2$, crystallises in needles, melts at 260°, and is insoluble in water. *Oxalylparaphenetidine* crystallises in six-sided tablets, melts at 110°, and dissolves in hot water, alcohol, and glacial acetic acid. *Tartronyldiparanisidine* crystallises in large, lustrous laminæ, melts at 259°, and dissolves freely in alcohol and hot glacial acetic acid, but only sparingly in ether, chloroform, and benzene. *Tartronyldiparaphenetidine* forms large laminæ, melts at 271°, and resembles the preceding compound in solubility.

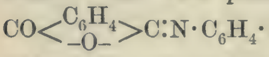
By heating such substituted amidophenols as have been described above with acid chlorides, compounds containing acid radicles substituted in the hydroxyl of the phenol are obtainable. The following instances are cited; the compounds are best crystallised from glacial acetic acid. *Phthalylparamidophenylic benzoate*,

$$OBz\cdot C_6H_4\cdot N⁚(CO)_2⁚C_6H_4\,;$$

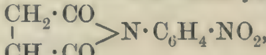
needles, melting at 256°. *Phthalylparamidophenylic butyrate*; needles, melting at 156°. *Phthalylparamidophenylic propionate*; needles, melting at 158°. *Phthalylparamidophenylic acetate*; needles, melting at 226°.

Succinylparamidophenylic benzoate, $OBz\cdot C_6H_4\cdot N:(CO)_2:C_2H_4$; needles, melting at 215°. *Succinylparamidophenylic propionate*; needles, melting at 178°. A. G. B.

Action of Phthalic and Succinic Chlorides on Compounds of the Type $R\cdot NH_2$. By Bronislaw Pawlewski (*Ber.*, 1896, **29**, 2679. Compare Abstr., 1895, i, 414).—By heating orthamidobenzoic acid with phthalic chloride, *phthalanilorthocarboxylic acid*,



$CO<\genfrac{}{}{0pt}{}{C_6H_4}{-O-}>C:N\cdot C_6H_4\cdot COOH$, is obtained; it melts and decomposes at 241—242°. Paranitraniline and succinic chloride yield pale yellowish *succinylparanitrophenylimide*,



$\begin{matrix}CH_2\cdot CO\\ | \\ CH_2\cdot CO\end{matrix}>N\cdot C_6H_4\cdot NO_2$, melting at 175°. C. F. B.

Aromatic Chlorophosphines and their Derivatives. By C. A. August Michaelis (*Annalen*, 1896, **293**, 261—325; **294**, 1—55. Compare Abstr., 1894, i, 586; this vol., i, 49).—[With Hubert Glaubitz.]—*Paratolylcyanophosphine*, $C_6H_4Me\cdot P(CN)_2$, obtained from paratolylchlorophosphine and silver cyanide, is a bright yellow, viscous liquid, which boils at 145° under a pressure of 50 mm.; *paratolylthiocyanophosphine*, $C_6H_4Me\cdot P(SCN)_2$, is a reddish-yellow liquid, which boils at 237—240° under a pressure of 40 mm.

Phenylic paratolylphosphonate, $C_6H_4Me\cdot PO(OPh)_2$, is obtained from tolyloxychlorophosphine and phenol (2 mols.), the mixture being heated at 120—130°; it is a colourless, viscous liquid, which exhibits feeble, blue fluorescence, and boils above 360°. The *chloride*, $C_6H_4Me\cdot PO(OPh)Cl$, is produced when one-half the quantity of phenol is employed; it is a white, crystalline mass, which melts at 55°, and boils above 360° without undergoing decomposition. *Silver phenylic paratolylphosphonate* and *phenylic paratolylphosphonamide*, $C_6H_4Me\cdot PO(OPh)\cdot NH_2$, have also been prepared, and the latter substance crystallises from ether and melts at 115—116°. The *phenylhydrazide* of monophenylic paratolylphosphonate crystallises in small, white needles, and melts at 173—174°; the *piperidide* is a yellow oil.

Paratolylic paratolylphosphonate, $C_6H_4Me\cdot PO(O\cdot C_6H_4Me)_2$, is a viscous liquid which boils above 360°; the *chloride* melts at 60°, and boils above 360° without undergoing change.

Phenylenic paratolylphosphonate, $C_6H_4Me\cdot PO:O_2:C_6H_4$, melts at 81°, forming a feebly fluorescent liquid which boils above 360°; the *chloride* is a colourless, viscuous liquid, which does not decompose when distilled above 360°.

Paratolylphosphondiamide, $C_6H_4Me\cdot PO(NH_2)_2$, crystallises in colourless, lustrous leaflets, and melts at 176°; this substance is not formed when tolyloxychlorophosphine is treated with ammonium carbonate, a compound being produced which melts at 74°, and is probably an *isomeride* of paratolylphosphonic acid (m. p. 189°), as it yields this product when treated with boiling water. The *dianilide*, $C_6H_4Me\cdot PO(NHPh)_2$, crystallises in small, nacreous needles, and melts at 209°. The *toluidide* forms slender, snow-white needles, and melts at 237°, and the *monotoluidide*, $C_6H_4Me\cdot PO(OH)\cdot NH\cdot C_6H_4Me$, is a white powder which melts at 208°; the *phenylhydrazide* forms slender needles, and melts at 171°.

*Aniline-*n*-tolylphosphonic acid*, $C_6H_4Me\cdot PO(OH)\cdot NHPh$, is obtained as chloride along with the foregoing anilide when tolyloxychlorophosphine is heated with aniline hydrochloride; it is a white powder, which melts at 150°, and is decomposed when dissolved in alcohol or glacial acetic acid. The *copper* salt is a bright blue powder; the *phenylic* salt melts at 59°, forming a very viscous, highly-refractive oil, which boils at 283° under a pressure of 48 mm.

[With E. PIPER.]—*Nitroparatolylphosphonic acid*,

$$NO_2\cdot C_6H_3Me\cdot PO(OH)_2,$$

is obtained by heating paratolylphosphonic acid with fuming nitric acid for 2 hours in a reflux apparatus; it crystallises in aggregates of pale yellow needles, and melts at 191°. The *barium* salt forms yellowish leaflets, and contains $2H_2O$, and the *calcium* salt contains $1H_2O$; the *lead*, *copper*, and *silver* salts are anhydrous, and the *ethylic* salt is liquid.

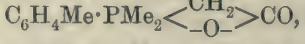
Dinitroparatolylphosphonic acid is obtained by heating the phosphonic acid with a mixture of concentrated and fuming nitric acids for 3 hours on the water bath; it crystallises from water in yellowish leaflets, and melts at 251°. The *barium* salt contains $2H_2O$, and the *lead* salt is anhydrous.

Amidoparatolylphosphonic acid is formed on reducing the nitro-derivative with tin and hydrochloric acid, and crystallises from alcohol in lustrous needles; it rapidly darkens in the atmosphere, and melts indefinitely at 270—290°. The *silver* and *lead* salts are amorphous, and the *ethylic* salt is a yellow liquid. The action of nitrous acid in presence of hydrochloric acid gives rise ultimately to trichlorotoluquinone, along with a substance which is probably tartronic acid.

Parabenzophosphonic acid, $COOH\cdot C_6H_4\cdot PO(OH)_2$, was obtained by Michaelis and Paneck on oxidising paratolylphosphonic acid with potassium permanganate. The *hydrogen calcium* and *hydrogen barium* salts are anhydrous, and the *copper* salt is a bright blue, crystalline substance, containing $1\frac{1}{2}H_2O$. The *dihydrogen ethylic* salt crystallises in long, colourless needles, and melts at 78°; the *hydrogen silver ethylic* salt forms snow-white crystals. The *monamide* crystallises in small needles, melting above 300°, and forms the *silver* salt, which is a white powder very sensitive to light. The *anilide* separates from alcohol in small, white crystals, and melts at 242°.

[With MORITZ G. MIETHING.]—*Paratolyldimethylphosphine oxide*, $C_6H_4Me\cdot PMe_2O$, is obtained by suspending paratolyldimethylphosphine (Czimatis, Abstr., 1883, 57) in much water, and adding a slight excess of mercuric oxide; it is a hygroscopic, crystalline mass, and melts at 95°. The *nitro*-derivative forms yellow prisms, melting at 175°, and yields a *mercurichloride*, which crystallises from water in slender, white needles, and melts at 127°.

Dimethylphosphine-oxide-parabenzoic acid, $COOH\cdot C_6H_4\cdot PMe_2O$, is produced on oxidising paratolyldimethylphosphine oxide with potassium permanganate; it separates from alcohol and ether in colourless crystals, melts at 240°, and boils above 360° under a pressure of 15 mm. The *mercurichloride* crystallises in beautiful white needles, and melts at 154°, the *aurochloride* forms colourless, rhombic plates, and the *platinochloride* crystallises in colourless plates, and melts at 234°. The *ammonium* salt melts and decomposes at 212°, the *silver* salt forms colourless crystals, and the *copper* salt is a bluish-green powder. The *chloride* is a liquid, and, when treated with aniline, yields the *anilide*, which crystallises from alcohol in nacreous leaflets, and melts at 235°.



Tolyldimethylphosphobetaïne, $C_6H_4Me\cdot PMe_2{<}\substack{CH_2\\ -O-}{>}CO$, is obtained by the action of silver oxide on the *hydrochloride* of the ethylic salt, $C_6H_4Me\cdot PMe_2Cl\cdot CH_2\cdot COOEt$, which is formed by the action of ethylic chloracetate on tolyldimethylphosphine, separating as a hygroscopic crystalline powder, which melts at 153°; the *platinochloride* of the ethylic salt forms slender, yellowish-red needles, and melts at 200°. The *betaïne* itself melts at 206°, and the *hydrochloride* at 172°, whilst the *platinochloride* crystallises from hot water in small needles, and melts at 220°.

Tolyldiethylphosphine oxide, $C_6H_4Me\cdot PEt_2O$, forms hygroscopic crystals, and melts at 74°; the *mercurichloride* contains $1H_2O$, and melts at 135°. The *nitro*-derivative is an oil, forming a *mercurichloride*, which melts at 105°.

Diethylphosphine-oxide-parabenzoic acid, $COOH\cdot C_6H_4\cdot PEt_2O$, is an oil which distils under a pressure of 15 mm. without undergoing change; the *anilide* crystallises in leaflets, and melts at 198°, and the *mercurichloride* at 134°. The *betaïne* is a hygroscopic mass, and yields a *platinochloride*, which crystallises from hot water in yellow needles, and melts at 157°; the *ethylic* salt of the betaïne is a liquid, forming the *hydrochloride*, which melts at 96°.

[With Luis da Rocha Schmidt.]—Orthotolylchlorophosphine is a colourless, highly-refractive liquid, having a sp. gr. = 1·3067 at 18·5°, and boils at 244°.

Orthotolyltetrachlorophosphine, $C_6H_4Me\cdot PCl_4$, is a white, crystalline substance, and melts at 63—66°. *Orthotolyloxychlorophosphine*,

$$C_6H_4Me\cdot POCl_2,$$

is obtained from the tetrachloride by means of sulphurous anhydride, and forms a colourless liquid having a sp. gr. = 1·3877 at 18·5°, and boils at 273°.

Orthotolylphosphine oxide, $C_6H_4Me\cdot PO_2$, crystallises from benzene in short prisms. *Ammonium* orthotolylphosphinite is a crystalline salt, becoming brown on exposure to air, and the *barium* salt contains $1H_2O$; the *copper* and *lead* salts are anhydrous, and the *anilide* crystallises in white needles, and melts at 234°.

Chlororthotolylphosphonic acid [Me : P : Cl = 1 : 2 : 4] is produced by the action of chlorine on orthotolylphosphonic acid, and separates from dilute alcohol in small crystals, melting at 205°; the *silver* salt is amorphous. *Dichlororthotolylphosphonic acid* crystallises in slender needles, and melts at 240°; the *silver* salt is a white powder.

[With E. Piper.]—*Nitro-orthotolylphosphonic acid*,

$$[Me : P : NO_2 = 1 : 2 : 4],$$

is obtained more readily than the para-compound, being formed when a solution of the phosphonic acid in fuming nitric acid is evaporated on the water bath; it crystallises from water in pale yellow needles, and melts at 174°. The *barium* and *calcium* salts are anhydrous.

Amidorthotolylphosphonic acid, obtained by reducing the nitro-compound, crystallises in needles which quickly become brown, and softens at 280—300°, above which temperature it decomposes; the *barium* salt is a reddish-brown powder, sparingly soluble in water, and the *calcium* salt is also moderately soluble.

Orthobenzophosphonic acid, obtained by oxidising orthotolylphosphonic acid with potassium permanganate, separates from water in small crystals, melting at 172°; when gently heated in small quantity, it sublimes for the most part without undergoing change. The *silver* salt is a white substance, which is sensitive to light; the *chloride* melts at 54°

Orthotolyldiethylphosphine, $C_6H_4Me\cdot PEt_2$, is a mobile, colourless liquid of penetrating odour, and boils at 263°. The *methiodide* crystallises from water in colourless needles, and melts at 98°; the *ethiodide* crystallises from alcohol, and melts at 162°.

[With William Berghegger.]—*Metatolylchlorophosphine* is prepared by heating small quantities of 1:3-mercuryditolyl (Abstr., 1895, i, 368) with phosphorus trichloride (10 parts) in sealed tubes at 200° for 12 hours; it is a dense, colourless liquid, which boils at 235°, and has a sp. gr. = 1·282 at 22°.

Metatolyltetrachlorophosphine is a viscous oil, which becomes crystalline below 0°. *Metatolyloxychlorophosphine* boils at 275°, and has a sp. gr. = 1·3533 at 18°.

Ammonium metatolylphosphinite crystallises in lustreless, white needles, and the *potassium* salt is deliquescent; the *barium* salt forms stellar aggregates of needles, and the *phenylhydrazine* salt, crystallising in yellow needles, melts and decomposes at 131°.

Metatolylphosphonic acid, $C_6H_4Me\cdot PO(OH)_2$, crystallises from water in lustreless, white needles, and melts at 116—117°. The *hydrogen potassium* salt forms white needles, and the *trihydrogen potassium* salt, white leaflets; the *barium*, *silver*, and *hydrogen silver* salts are anhydrous.

Chlorometatolylphosphonic acid [Me:P:Cl = 1:3:4] is formed when a stream of chlorine is passed into an aqueous solution of metatolylphosphonic acid for 20 minutes; it crystallises from water in small, white needles, and melts at 176°. The *silver* salt is a white powder, and resists the action of light. Trichlorotolylphosphonic acid

$$[Me:P:Cl_3 = 1:3:2:4:5],$$

is obtained by prolonged action of the halogen, and crystallises in needles or leaflets, melting at 220°; when heated above this temperature, it yields 1:2:4:5-trichlorotoluene, and is, therefore, identical with trichlorotolylphosphinic acid described by Michaelis and Lange (this Journal, 1876, i, 392).

Bromometatolylphosphonic acid [Me:P:Br = 1:3:4] crystallises from water in white needles, and melts at 198°; the *silver* salt is amorphous.

Metabenzophosphonic acid is obtained by oxidising metatolylphosphonic acid, and crystallises from alcohol in small, white needles, melting at 245—246°; the *silver*, *lead*, and *barium* salts are anhydrous, and the *chloride* is a white, crystalline substance, which melts at 61°, and boils at 360°.

[With Moritz Lewschinsky].—*Parethylphenylchlorophosphine* (*ethylbenzenechlorophosphine*), $C_6H_4Et\cdot PCl_2$, is prepared from ethylbenzene, phosphorus trichloride and aluminium chloride, and forms a colourless, highly-refractive liquid, which boils at 250—252°, and has a sp. gr. = 1·227 at 17°.

Ethylbenzenetetrachlorophosphine is obtained by the action of chlorine on the foregoing substance, and forms a white, crystalline mass, melting at 51°. *Ethylbenzeneoxychlorophosphine* is a colourless liquid which boils at 294°, and has a sp. gr. = 1·29 at 16°.

Ethylbenzenephosphinous acid, $C_6H_4Et{\cdot}PHO{\cdot}OH$, is produced when the chlorophosphine is treated with water, and the liquid evaporated; it separates in crystals, and melts at 63—64°. The *ammonium* salt forms lustrous, quadratic leaflets, and the *barium* salt is a crystalline powder containing $1H_2O$; the copper salt is a bluish-green, crystalline powder, and the *phenylhydrazine* salt separates from hot water in lustrous, yellowish-white leaflets, and melts at 133°.

Ethylbenzenephosphonic acid crystallises from water in slender, lustrous needles, and melts at 164°; the *hydrogen ammonium* salt crystallises with difficulty, and the *hydrogen phenylhydrazine* and *trihydrogen potassium* salts crystallise from water. The *barium* salt forms lustrous needles, and contains $3H_2O$; the *copper* salt is greenish-white, and contains $1H_2O$, and the *silver* salt is a white, crystalline powder. Ethylbenzenephosphinic acid is immediately oxidised by potassium permanganate, in alkaline solution, yielding benzophosphinic acid, carbonic anhydride, and water.

Phosphino-ethylbenzene, $C_6H_4Et{\cdot}PO_2$, is obtained by dissolving ethylbenzene-phosphinic acid in benzene and heating the solution with ethylbenzeneoxychlorophosphine on the water bath in a reflux apparatus; it is exceedingly hygroscopic, and forms small, white crystals, which melt at 68°.

Di-ethylbenzenephosphonic acid, $(C_6H_4Et)_2PO{\cdot}OH$, is a bye-product in the preparation of ethylbenzenephosphinous acid, and is isolated in the form of the *copper* salt; the *silver* salt is amorphous.

Ethylbenzenephosphine, $C_6H_4Et{\cdot}PH_2$, is a transparent, highly-refractive liquid which boils at 200°; the *platinochloride* is a golden yellow, crystalline powder, and the *hydriodide* separates from water in lustrous, white crystals, melting at 118°.

Ethylbenzenediethylphosphine, $C_6H_4Et{\cdot}PEt_2$, is a colourless, highly-refractive liquid, having a penetrating odour; it boils at 268—270°, and has a sp. gr. = 0·929 at 17°. The *platinochloride* is reddish-white, and the *methiodide* crystallises in long, white needles, and melts at 135°; the *ethiodide* forms white needles, and when heated is resolved into its components without undergoing fusion.

Ethylbenzenephosphinophenylhydrazone, $C_6H_4Et{\cdot}P{:}N{\cdot}NHPh$, is obtained by the action of ethylbenzenechlorophosphine on phenylhydrazine dissolved in ether; it is a white crystalline powder, and melts at 139°.

[With Fritz Rothe and R. Uster].—*ψ-Cumylchlorophosphine*, $C_6H_2Me_3{\cdot}PCl_2$ $[Me_3{:}PCl_2 = 1{:}2{:}4{:}5]$, obtained from ψ-cumene, phosphorus trichloride, and aluminium chloride, is a colourless, highly-refractive liquid, which boils at 280°, and has a sp. gr. = 1·2356 at 20°; it is also produced when the mercury derivative corresponding with symmetrical bromo-ψ-cumene (Abstr., 1895, i, 368) is heated with phosphorus trichloride in sealed tubes at 230—240°. *ψ-Cumyltetra-*

chlorophosphine, $C_6H_2Me_3\cdot PCl_4$, is a greenish-white crystalline mass, and melts at 75°. *ψ-Cumyloxychlorophosphine*, $C_6H_2Me_3\cdot POCl_2$, is crystalline and colourless; it melts at 63°, and boils at 307—308°.

ψ-Cumylphosphinous acid, $C_6H_2Me_3\cdot PHO\cdot OH$, is produced by the action of water on the chlorophosphine, and crystallises from alcohol in rhombic leaflets; it melts at 128°, and undergoes no change when exposed to the air. The *potassium*, *lead*, and *copper* salts are anhydrous, and the *barium* salt contains $3H_2O$; the *phenylhydrazine* salt crystallises in small white needles, and melts at 180°.

ψ-Cumylphosphonic acid, $C_6H_2Me_3\cdot PO(OH)_2$, is obtained by the action of water on the tetrachloro- and oxychloro-phosphines, and crystallises from water in white needles; it melts at 212°, and is sparingly soluble in cold water. The *hydrogen potassium*, *hydrogen barium*, and *silver* salts are anhydrous; the *hydrogen nickel* salt, with $4H_2O$, crystallises in lustrous, green leaflets. The *phenylic* salt melts at 62·5°, and boils above 360°; the *dianilide*, $C_6H_2Me_3\cdot PO(NHPh)_2$, crystallises from dilute acohol in lustrous needles, and melts at 197°. *Trianilido-ψ-cumylphosphonium chloride*, $C_6H_2Me_3\cdot(NHPh)_3Cl$, obtained by heating ψ-cumyltetrachlorophosphine with aniline hydrochloride at 170—180°, melts at 247°; the *bromide*, *iodide*, and *nitrate* melt at 259°, 220°, and 224—225° respectively, whilst the *hydroxide*, which is indifferent towards litmus, melts at 203·5°. The *phenylhydrazide* of ψ-cumylphosphinic acid, $C_6H_2Me_3\cdot PO(N_2H_2Ph)_2$, crystallises in small, lustrous needles, and melts at 208°; it reduces Fehling's solution when heated.

Chloro-ψ-cumylphosphonic acid $[Me_3:P:Cl = 1:2:4:5:6]$ is produced when chlorine is passed into a solution of ψ-cumylphosphonic acid dissolved in glacial acetic acid, and crystallises in white, lustrous needles, melting at 235°; when treated with fuming nitric acid at low temperatures, it yields nitrochloro-ψ-cumylphosphonic acid, the hot acid converting it into dinitrochloro-ψ-cumene. The *hydrogen phenylhydrazine* salt crystallises from alcohol in small needles, and melts at 197·5°. 6 : 3-*Chloronitro-ψ-cumylphosphonic acid* crystallises from water in long, lustrous, pale yellow needles, and, when slowly heated, melts and decomposes at 227—228°. 3 : 6-*Dinitro-ψ-cumylphosphonic acid* forms small, white needles, and decomposes at 239° when slowly heated; if the temperature is raised rapidly, the nitro-acids explode. The *hydrogen phenylhydrazine* and *hydrogen aniline* salts of the dinitro-acid melt and decompose at 240° and 273° respectively, the *copper* salt crystallises in greenish needles containing $1H_2O$, and the *silver* and *hydrogen silver* salts crystallise from water.

Xylophosphonic acid, $COOH\cdot C_6H_2Me_2\cdot PO(OH)_2$ $[=1:2:4:5]$, obtained by oxidising ψ-cumylphosphonic acid in alkaline solution with potassium permanganate, melts at 258°, and, when heated above this temperature, yields metaphosphoric and xylenecarboxylic acids. The *silver* salt is sensitive to light. *Methylphthalophosphonic acid*,

$$(COOH)_2C_6H_2Me\cdot PO(OH)_2\ [?=1:4:3:6],$$

is produced when the oxidation with permanganate is performed under modified conditions; it is a yellowish, hygroscopic powder, which melts at 185—190°; the *silver* salt is colourless.

Di-ψ-cumylphosphonic acid, $(C_6H_2Me_3)_2PO\cdot OH$, is obtained on treating with water the residue from the preparation of ψ-cumylchlorophosphine after extraction with light petroleum. It forms highly refractive crystals, belonging to the monoclinic system, the axial ratios being $a : b : c = 0{\cdot}96 : 1 : 0{\cdot}983$; $\beta = 113°$. The acid melts at 202—203°, and is converted at 240—250° into ψ-cumene and *phosphino-ψ-cumene*, $C_9H_{11}PO_2$, a white, crystalline powder, which melts at 80°. The *potassium* salt of di-ψ-cumylphosphonic acid contains $1H_2O$, and the ammonium salt $2H_2O$; the *barium*, *lead*, *silver*, *cobalt*, *nickel*, and *copper* salts are anhydrous, but the two last-named contain $10H_2O$ when crystallised from aqueous ether.

Di-xylophosphonic acid, $(COOH{\cdot}C_6H_2Me_2)_2PO{\cdot}OH$, is produced on oxidising di ψ-cumylphosphonic acid with potassium permanganate ; it melts at 185°, and the *silver* salt is not altered by exposure to light.

ψ-Cumylphosphine, $C_9H_{11}{\cdot}PH_2$, which is obtained when an alcoholic solution of ψ-cumylphosphinous acid is submitted to distillation in an atmosphere of carbonic anhydride, has a very disagreeable odour, and boils at 214–218° ; it is rapidly oxidised on exposure to air, ψ-cumylphosphinous acid being produced. The *platinochloride* is yellow, and the *diethyl* derivative has a penetrating odour, boils at 274—275°, and yields a red, crystalline *platinochloride* ; *methyldiethyl-ψ-cumylphosphonium iodide* crystallises from water in lustrous, rhombic plates, and melts at 160°.

Diphenoxy-ψ-cumylphosphine, $C_9H_{11}{\cdot}P(OPh)_2$, obtained by the action of ψ-cumylchlorophosphine on sodium phenoxide suspended in ether, is a viscous, colourless liquid, having a sp. gr. = 1·144 at 15°, and the refractive index = 1·5085 ; it boils at 283° under a pressure of 40 mm. Boiling water converts it into phenol and ψ-cumylphosphinous acid. *Diethoxy-ψ-cumylphosphine*, $C_9H_{11}{\cdot}P(OEt)_2$, is a colourless liquid, having the odour of the thiocarbimides ; it has a sp. gr. = 1·048 at 15°, the refractive index = 1·505, and it boils at 232—233° under a pressure of 100 mm.

[With BERNHARD HECKER.]—*Mesitylchlorophosphine*, $C_6H_2Me_3{\cdot}PCl_2$, $[Me_3 : PCl_2 = 1 : 3 : 5 : 4]$, is prepared from mesitylene, phosphorus trichloride, and aluminium chloride, and crystallises in transparent plates a centimetre in length ; it melts at 35—37°, forming a highly-refractive, colourless liquid, which boils at 273—275°, and has a sp. gr. = 1·205 at 15°. *Mesityltetrachlorophosphine*, $C_6H_2Me_3{\cdot}PCl_4$, melts at 70°. *Mesityloxychlorophosphine*, $C_6H_2Me_3{\cdot}POCl_2$, forms large, transparent crystals ; it melts at 92—93°, and boils above 360°.

Mesitylphosphinous acid, $C_6H_2Me_3{\cdot}PHO{\cdot}OH$, crystallises from water in lustrous needles, and melts at 147° ; the *potassium*, *ammonium*, *calcium*, and *copper* salts are crystalline and anhydrous. The *phenylhydrazine* salt melts and decomposes at 132°, and the *aniline* salt crystallises in long, yellowish needles ; the *barium* salt contains $6H_2O$, and crystallises in long needles, which rapidly effloresce on exposure.

Mesitylphosphonic acid, $C_6H_2Me_3{\cdot}PO(OH)_2$, crystallises from dilute alcohol in long, colourless needles, and melts at 167° ; the *hydrogen ammonium* and *silver* salts are anhydrous, whilst the *barium* salt contains $1H_2O$, and the *nickel* salt $8H_2O$. *Phosphinomesitylene*,

$$C_6H_2Me_3{\cdot}PO_2,$$

is produced when the phosphonic acid is heated with benzene and the oxychlorophosphine in a reflux apparatus at 40° ; it separates from chloroform in small crystals, and melts and decomposes at 215—216°.

β-Xylophosphonic acid, $COOH\cdot C_6H_2Me_2\cdot PO(OH)_2$, is obtained on oxidising mesitylphosphonic acid with potassium permanganate; it is amorphous, and melts at 245°, yielding metaphosphoric and mesitylenic acids at higher temperatures. The *silver* salt is decomposed by light. *Methylisophthalophosphonic acid*, $(COOH)_2C_6H_2Me\cdot PO(OH)_2$, is also formed during oxidation, and is very hygroscopic; it sinters at 215° and melts at 255°, yielding metaphosphoric and uvitic acids when heated above this temperature. The *silver* salt resists the action of light.

Mesitylphosphine, $C_6H_2Me_3\cdot PH_2$, is produced on submitting mesitylphosphinous acid to dry distillation in an atmosphere of carbonic anhydride; it forms colourless needles which melt at 40°, and under a pressure of 25 mm. it boils at 125°. The *platinochloride* forms orange crystals, and the *diethyl* derivative boils at 170°, and forms an orange *platinochloride*; *mesitylmethyldiethylphosphonium iodide* crystallises in colourless, lustrous needles, and melts, decomposing, at 125°. The *phenylhydrazone*, $C_9H_{11}P{:}N\cdot NHPh$, crystallises in small, lustrous needles, and melts at 135°.

[With OSWALD MEYER.]—*Cumylchlorophosphine*, $CHMe_2\cdot C_6H_4\cdot PCl_2$, is obtained from cumene, phosphorus trichloride, and aluminium chloride; it is a colourless liquid which boils at 268—270°, and has a sp. gr. = 1·190 at 12°. *Cumyltetrachlorophosphine*, $CHMe_2\cdot C_6H_4\cdot PCl_4$, is a white, crystalline mass which melts at 53—55°. *Cumyloxychlorophosphine*, $CHMe_2\cdot C_6H_4\cdot POCl_2$, melts at 35°, and boils at 183° under a pressure of 35 mm.

Cumylphosphinous acid, $CHMe_2\cdot C_6H_4\cdot PHO\cdot OH$, is a viscous oil, which dissolves sparingly in water; the *barium* salt contains $1H_2O$, the *phenylhydrazine* salt melts at 161°, and the *hydrogenphenylhydrazine* salt at 135°.

Cumylphosphonic acid, $CHMe_2\cdot C_6H_4\cdot PO(OH)_2$, produced on decomposing the tetrachloride with water, crystallises from cymene in lustrous prisms, melting at 139°; the *barium* and *silver* salts are anhydrous, and the *phenylhydrazine* salt crystallises in pale yellow leaflets, and melts at 172°.

Hydroxyisopropylphenylphosphonic acid, $OH\cdot CMe_2\cdot C_6H_4\cdot PO(OH)_2$, obtained by oxidising cumylphosphonic acid with potassium permanganate, separates as an oil from the aqueous solution; at 105—120°, the acid loses water, yielding *phenylallylphosphonic acid*,

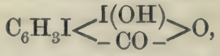
$$C_3H_5\cdot C_6H_4\cdot PO(OH)_2,$$

a white powder which melts at 250°.

Dicumylphosphonic acid, $(CHMe_2\cdot C_6H_4)_2PO\cdot OH$, is a bye-product in the preparation of cumylphosphonic acid, and remains after removing the latter by means of light petroleum; it is a white powder, which becomes brown when heated, but does not melt. The *copper* and *aluminium* salts are anhydrous.

Cymylchlorophosphine, $C_6H_3MePr^{\alpha}\cdot PCl_2$, boils at 275—278°; the *tetrachlorophosphine* is a viscous liquid. *Cymylphosphinous acid* is liquid, and the *barium* salt contains $1H_2O$. *Cymylphosphonic acid* is also liquid, and the *hydrogen silver* and *silver* salts are decomposed by light; the *phenylhydrazine* salt crystallises from alcohol, and melts at 156°. *Cumyldiethylphosphine* boils at 260—270°. M. O. F.

Behaviour and Oxidation of Tetriodoterephthalic Acid and Tri-iododiamidobenzoic Acid. By JACOB LÜTJENS (*Ber.*, 1896, **29**, 2833—2839).—It is well-known that, whilst orthoiodobenzoic acid readily yields an iodoso-derivative on oxidation, the isomeric meta- and para-acids fail to do so. This difference in behaviour is possibly connected with the fact that, on occasion, the orthoiodoso-acid acts as a compound having a structure $C_6H_4<\genfrac{}{}{0pt}{}{I(OH)}{-CO-}>O$, which the isomeric acids are unable to assume. On this supposition, diorthoiodobenzoic acid on oxidation should yield only a moniodoso-derivative,



$$C_6H_3I<\genfrac{}{}{0pt}{}{I(OH)}{-CO-}>O,$$

and in like manner tetriodoterephthalic acid should yield a di-iodoso-acid.

2 : 4 : 6-*Tri-iodo*-3 : 5-*diamidobenzoic acid* is formed when a solution of dimetamidobenzoic acid in sulphuric acid is treated with one of iodine and iodic acid in caustic soda. It crystallises from hot, dilute alcohol in grey, felted needles. Attempts to eliminate its amido-groups were unsuccessful.

The author describes briefly the following salts of tetriodoterephthalic acid : The *calcium* salt, $C_6I_4(COO)_2Ca + 2H_2O$; the *strontium* salt, $C_6I_4(COO)_2Sr + 8H_2O$; the *barium* salt, $C_6I_4(COO)_2Ba + 4H_2O$; the *magnesium* salt, $C_6I_4(COO)_2Mg + 6H_2O$, and the *cadmium* salt,

$$C_6I_4(COO)_2Cd + 4H_2O,$$

are readily soluble in water; the *copper* salt, $C_6I_4(COO)_2Cu + 3H_2O$, forms blue-green crystals, and is sparingly soluble in water; the *methylic* salt, $C_6I_4(COOMe)_2$, crystallises in white needles, melting at 310—312°, the *ethylic* salt, $C_6I_4(COOEt)_2$, melts at 262·5°, and the *propylic* salt, $C_6I_4(COOPr)_2$, at 239°. The *chloride*, $C_6I_4(COCl)_2$, crystallises from chloroform, and melts at 279° ; the properties of the latter are in accordance with those of other diortho-substituted benzoic acids, the substance being characterised by its excessive stability towards alkalis and hot water.

Di-iodosodi-iodoterephthalic acid, $C_6I_2(<\genfrac{}{}{0pt}{}{I(OH)}{-CO-}>O)_2$, is produced when tetriodoterephthalic acid is warmed with a large excess of fuming nitric acid, and is most readily purified by means of its sodium salt. It is a a lemon-yellow powder insoluble in the ordinary media, and has very feeble acid properties, being precipitated from solutions of its salts by carbonic anhydride.

A. L.

Addition of Hydrogen Cyanide to Unsaturated Carboxylic Acids. By JULIUS BREDT and J. KALLEN (*Annalen*, 1896, **293**, 338—371).—*Ethylic cyanobenzylmalonate*, $CN\cdot CHPh\cdot CH(COOEt)_2$, is prepared by cautiously adding 33 per cent. hydrochloric acid to an alcoholic solution of ethylic benzylidenemalonate mixed with aqueous potassium cyanide, the liquid being well cooled during the operation ; it crystallises in needles melting at 48·5°, and yields phenylcyanopropionic acid when hydrolysed with baryta.

Phenylcyanopropionic acid, $CN\cdot CHPh\cdot CH_2\cdot COOH$, is obtained by heating alcoholic ethylic benzylidenemalonate with aqueous potassium cyanide on the water bath, and crystallises from dilute alcohol in slender needles, melting at 150° ; the *ethylic* salt is produced when half the quantity of potassium cyanide and a much larger proportion of alcohol are employed, and forms a colourless liquid, which boils at 176° under a pressure of 16 mm. The *calcium* and *barium* salts crystallise in needles containing $3H_2O$, and the *silver* salt is a white, amorphous powder. When phenylcyanopropionic acid is hydrolysed with potash, phenylsuccinic acid is produced ; the anhydride melts at 150° (compare Spiegel, *Annalen*, 1883, **219**, 30).

Ethylic β-cyanobutyrate, $CN\cdot CHMe\cdot CH_2\cdot COOEt$, is obtained on heating ethylic ethylidenemalonate, dissolved in alcohol, with aqueous potassium cyanide for 7 hours at 60° ; it is a colourless, mobile liquid having a pleasant odour, and boils at 105—106°, under a pressure of 14 mm. Hydrolysis with baryta converts it into pyrotartaric acid.

Hydroalantolactonitrile, $CN\cdot C_{15}H_{21}O_2$, is produced when alantolactone (Abstr., 1895, i, 555) is dissolved in alcohol and heated with aqueous potassium cyanide for 12 hours in a reflux apparatus ; it crystallises in silvery scales, and melts at 132°.

Hydroalantolic acid nitrile, $CN\cdot C_{14}H_{21}(OH)\cdot COOH$, is obtained in the form of the *sodium* salt, when the lactone is treated with alcoholic sodium ethoxide ; the salt crystallises in stout needles, and yields the lactone when treated with acids. The *barium* and *calcium* salts are anhydrous, and the *silver* salt is amorphous. The *amine*, $NH_2\cdot CH_2\cdot C_{15}H_{21}O_2$, obtained on reducing hydroalantolactonitrile by adding sodium to the boiling solution in absolute alcohol, crystallises from dilute alcohol in aggregates of needles; it melts and decomposes at 171°, and the *platinochloride* is a bright yellow substance insoluble in ether and water.

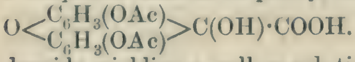
Hydroalantolactonecarboxylic acid, $C_{15}H_{21}O_2\cdot COOH$, is formed when hydroalantolactonitrile is heated on the water bath with alcoholic potash so long as ammonia is liberated ; it crystallises from dilute alcohol in colourless, prismatic needles, melts at 137°, and boils at 250° under a pressure of 14 mm. The *sodium*, *barium*, and *calcium* salts are anhydrous, and the *silver* salt crystallises from boiling water.

Salts of hydroalantodicarboxylic acid, $OH\cdot C_{14}H_{21}(COOH)_2$, are obtained by hydrolysing the foregoing lactonic acid with alkalis, but on acidifying the solution, separation of the lactone takes place ; the *sodium* salt is very hygroscopic, and crystallises in small needles insoluble in alcohol. The *barium* and *calcium* salts dissolve with difficulty in water, and the *lead* salt is an amorphous powder insoluble in cold and hot water.

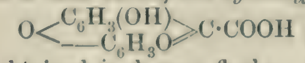
Orthohydroxyphenylsuccinic acid, $OH\cdot C_6H_4\cdot CH(COOH)\cdot CH_2\cdot COOH$, is produced on heating an alcoholic solution of coumarin with aqueous potassium cyanide for 6 hours in a reflux apparatus ; when rapidly heated, it melts at 150°, water being eliminated and the anhydride produced, this change taking place at 135° when that temperature is maintained for a considerable period. The aqueous solution develops a violet coloration with ferric chloride ; the *calcium* and *barium* salts are anhydrous. The *anhydride* melts at 134°, and boils at 200° under a pressure of 14 mm, a portion undergoing decomposition ; the *acetyl* derivative of the anhydride crystallises from a mixture of chloroform and ether, and melts at 90°. M. O. F.

Condensation of Tannins with Formaldehyde. By C. EMANUEL MERCK (*Chem. Centr.*, 1896, i, 560; from *Ber. ü. d. Jahr.*, 1895, 14—19).—By treating plant extracts with formaldehyde in presence of hydrochloric acid, the tannins are easily withdrawn in the form of condensation products, which are named *tannoforms*. *Tannoform*, $CH_2(C_{14}H_9O_9)_2$, prepared by the condensation of tannin with formaldehyde, is a reddish-white powder which decomposes at 230°. It is soluble in alcohol and in dilute alkalis, with the latter forming a yellow or brownish-red solution, from which it is precipitated by acids. In warm, concentrated sulphuric acid, it dissolves, with production of a brown colour, and on further heating this turns green and then blue. With alcohol, either the green or the blue solution becomes first blue and then wine-red. *Quercitannoform*, $CH_2(C_{14}H_{13}O_7)_2 + H_2O$, prepared from oak bark tannin and formaldehyde, is a reddish-yellow powder, which blackens at 275°; it is insoluble in water, ammonia, and sodium hydroxide, and the brown colour of its solution in concentrated sulphuric acid is not affected by alcohol.

Quebrachitannoform, $CH_2(C_{26}H_{24}O_9)_2O$ or $CH_2(C_{26}H_{22}O_9)_2O$. *Rhatany tannoform*, $CH_2(C_{20}H_{16}O_7)O$, prepared from Rhatany tannin and formaldehyde with elimination of 4 molecules of water, is a yellowish-brown powder; its brownish-red solution in concentrated sulphuric acid rapidly turns red. *Myrobalans tannoform*, prepared from myrobalan tannin and formaldehyde, is a yellowish-brown powder with properties similar to those of tannoform, but its solution in concentrated sulphuric acid, on warming, becomes first green and then black. Like myrobalan tannin itself, it contains a little gallic acid and a considerable quantity of ellagic acid. This tannoform is an excellent protective against decubitus and hyperidrosis, and its effect is very different from that of tannin. E. W. W.



Oxidation of Diacetylcitraconfluoresceïn. By JOHN T. HEWITT and FRANK G. POPE (*Ber.*, 1896, **29**, 2824—2827).—The ethers of citraconfluoresceïn do not yield fluorone compounds when treated with alkaline potassium permanganate solution, owing to the readiness with which they suffer hydrolysis. Diacetylcitraconfluoresceïn, however, is oxidised by a hot solution of chromic acid in glacial acetic acid, yielding a *compound* difficult to purify, but which doubtless has the constitution $O<\begin{matrix}C_6H_3(OAc)\\C_6H_3(OAc)\end{matrix}>C(OH)\cdot COOH$. It is readily soluble in sodium hydroxide, yielding a yellow solution; this darkens on heating, and, if an acid is then added, the *hydroxyfluoronecarboxylic acid*,



$$O<\begin{matrix}C_6H_3(OH)\\C_6H_3O\end{matrix}>C\cdot COOH$$ [C:OH:O = 1:3:6; C:O:O = 1:3:6],

is obtained in brown flocks. This acid, if moist, dissolves somewhat readily in acetone, and is deposited from it as a heavy, brown, crystalline powder; it is very sparingly soluble in dry organic solvents, but dissolves readily in alkalis, and shows no tendency to form a lactone, hence the hydroxyl-group is in the para-position relatively to the carbon atom of the pyrone nucleus. The *ammonium* salt of the acid yields characteristic red precipitates with various metallic salts, that produced by silver nitrate having the composition $C_{14}H_7O_5Ag$. A. L.

The Colour Base $(C_{15}H_{11}N)_x$ from Benzylphthalimidine. By SIEGMUND GABRIEL and ROBERT STELZNER (*Ber.*, 1896, **29**, 2743—2746. Compare Abstr., 1888, 143).—This substance, the molecular formula and constitution of which have not yet been ascertained, is converted by nitric acid into nitrobenzylidenephthalimidine (Abstr., 1885, 903, 1231). Chlorine converts the base into *β-dichloro-a-deoxybenzoïnorthocarboxylamide*, $CPhCl_2\cdot CO\cdot C_6H_4\cdot CO\cdot NH_2$, which can also be obtained by the action of chlorine on deoxybenzoïncarboxylamide. It crystallises in stellate groups of flat prisms, and melts, with evolution of gas, at 197°. The chloro-compound is reduced by hydriodic acid and phosphorus to benzylphthalimidine. When it is heated at 140° with acetic and hydrochloric acids, benzilorthocarboxylic acid is produced. When the chloro-compound is dissolved in normal alkali and the solution gently warmed, crystals of dihydrodiphthalyldiimide (Abstr., 1893, i, 372) are deposited. Concentrated potash (33 per cent.) converts it in the cold into a substance of the formula $C_{15}H_{11}NO_2$, which is also formed as a bye-product in the reduction of nitrobenzylidenephthalide (Abstr., 1888, 143). Finally, the chloro-compound is decomposed, with evolution of ammonia and formation of benzoic and phthalic acids when it is boiled with 10 per cent. potash. A. H.

Constitution of the Colour Bases of the Triphenylmethane Series. By HUGO WEIL (*Ber.*, 1896, **29**, 2677—2678).—A reply to von Georgievics (Abstr., 1896, i, 441, 690), upholding the author's previous statements (*ibid.*, 565). An interesting statement, made in support of the alleged stability of magenta in presence of alkalis, is that, from a solution of rosaniline carbonate (prepared by passing carbonic anhydride into a suspension of rosaniline in water), sodium chloride precipitates rosaniline hydrochloride, whilst the now colourless solution is alkaline from the presence of sodium carbonate.

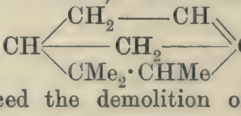
C. F. B.

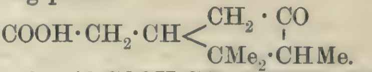
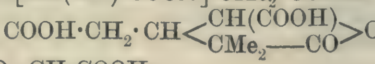
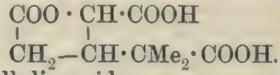
Hydroxy-derivatives of Tetramethyldiamidotriphenylmethane. By EMIL VOTOČEK (*Chem. Centr.*, 1896, i, 544; from *Listy Chem.*, 1895, 221—237).—The author obtained crystalline leuco-bases of dyes by the condensation of Michler's ketone with various phenols, namely, phenol, catechol, resorcinol, quinol, and pyrogallol. By oxidation of these bases, dichroic solutions of dyes are obtained, whilst the acetyl derivatives on oxidation yield green dyes which turn violet or blue on addition of alkalis. With para-amidophenol, no condensation could be effected. E. W. W.

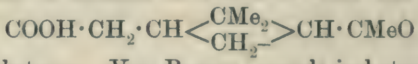
History of Madder Dyestuffs. By CARL T. LIEBERMAN and SIEGFRIED FRIEDLÄNDER (*Ber.*, 1896, **29**, 2851—2854). — Runge (*Monogr. des Krapps und der Krappforbstoffe*, 1835) maintained that the madder dyes, obtained by Robiquet and Colin, &c., were impure substances, but regarded his own madder-red and madder-purple as chemical entities. The authors have examined samples of cloth coloured with Runge's dyes, and find that, whilst his madder red was pure purpurin, his madder-purple was impure, although rich in alizarin.

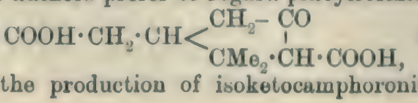
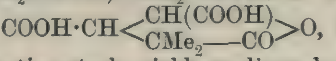
Samples of madder-dyeing from various localities were examined, and the results show that those from Avignon contained the largest proportion of alizarin, although contaminated with much purpurin.

The authors point out that the high proportion of alizarin in the French dyes accounts for the ease with which Robiquet and Colin achieved the isolation of pure alizarin. A. L.

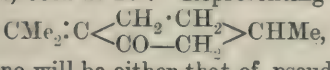
Pinene. By J. C. W. FERDINAND TIEMANN and FRIEDRICH W. SEMMLER (*Ber.*, 1896, **29**, 3027—3034).—The authors now claim to have established the formula  $\mathrm{CH}\left\langle\begin{matrix}\mathrm{CH_2}-\mathrm{CH}\\ \mathrm{CH_2}-\\ \mathrm{CMe_2}\cdot\mathrm{CHMe}\end{matrix}\right\rangle\mathrm{C}$ for the constitution of pinene, having traced the demolition of the hydrocarbon through the following phases.

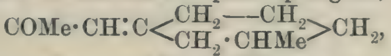
1. Pinonic acid;  $\mathrm{COOH}\cdot\mathrm{CH_2}\cdot\mathrm{CH}<\begin{matrix}\mathrm{CH_2}\cdot\mathrm{CO}\\ \mathrm{CMe_2}\cdot\mathrm{CHMe}\end{matrix}$.
2. Isoketocamphoric acid, $\mathrm{COOH\cdot CH_2\cdot CH(CH_2\cdot COOH)\cdot CMe_2\cdot CMeO}$.
3. Isocamphoronic acid, $\mathrm{COOH\cdot CH_2\cdot CH(CH_2\cdot COOH)\cdot CMe_2\cdot COOH}$.
4. Hydroxyisocamphoronic acid (salts),
$\mathrm{COOH\cdot CH_2\cdot CH[CH(OH)\cdot COOH]\cdot CMe_2\cdot COOH}$.
5. Isocamphoranic acid,  $\mathrm{COOH}\cdot\mathrm{CH_2}\cdot\mathrm{CH}<\begin{matrix}\mathrm{CH(COOH)}\\ \mathrm{CMe_2}-\mathrm{CO}\end{matrix}>\mathrm{O}$, or

$\begin{matrix}\mathrm{COO}\cdot\mathrm{CH}\cdot\mathrm{COOH}\\ \mathrm{CH_2}-\mathrm{CH}\cdot\mathrm{CMe_2}\cdot\mathrm{COOH}.\end{matrix}$
6. Dimethyltricarballylic acid,
$\mathrm{COOH\cdot CH(CH_2\cdot COOH)\cdot CMe_2\cdot COOH}$, and
7. Hydroxytrimethylsuccinic acid, $\mathrm{COOH\cdot CMe(OH)\cdot CMe_2\cdot COOH}$.

The widely different conclusion regarding the structure of pinene to which von Baeyer has been led, is attributed to the employment by that investigator of more vigorous agents in breaking down the molecule, leading to pinonic acid, $C_{10}H_6O_3$, pinoylformic acid, $C_{10}H_{14}O_5$, pinic acid, $C_9H_{14}O_4$, and norpic acid, $C_8H_{12}O_4$. The existence of a picean ring (this vol., i, 83) in the two last-named substances is not regarded by the authors as evidence of the presence of this complex in pinonic acid, because the behaviour of pinonic and pinoylformic acids towards oxidising agents differs widely from that of pinic and norpic acids; moreover, the production of isoketocamphoronic acid,
$\mathrm{COOH\cdot CH_2\cdot CH(CH_2\cdot COOH)\cdot CMe_2\cdot CMeO}$,
from pinonic acid is difficult to reconcile with the formula

$$\mathrm{COOH}\cdot\mathrm{CH_2}\cdot\mathrm{CH}<\begin{matrix}\mathrm{CMe_2}\\ \mathrm{CH_2}-\end{matrix}>\mathrm{CH}\cdot\mathrm{CMeO}$$
for the latter substance. Von Baeyer regards isoketocamphoronic acid as having the constitution $\mathrm{COOH\cdot CH_2\cdot CH(COOH)\cdot CMe_2\cdot CH_2\cdot CMeO}$, representing isocamphoronic acid by the expression
$\mathrm{COOH\cdot CH(CH_2\cdot COOH)\cdot CMe_2\cdot CH_2\cdot COOH}$,
but this is scarcely consistent with the glutaric character of the substance, and with its conversion into terpenylic acid, which is analogous to the transformation of α-dimethylglutaric acid into γ-isocaprolactone.

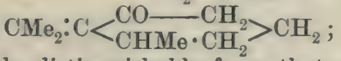
The authors prefer to regard pinoylformic acid as having the constitution  $\mathrm{COOH}\cdot\mathrm{CH_2}\cdot\mathrm{CH}<\begin{matrix}\mathrm{CH_2}-\mathrm{CO}\\ \mathrm{CMe_2}\cdot\mathrm{CH}\cdot\mathrm{COOH},\end{matrix}$ this being in agreement with the production of isoketocamphoronic acid when it is treated with sodium hypochlorite. When dimethyltricarballylic acid, $COOH\cdot CH(CH_2\cdot COOH)\cdot CMe_2\cdot COOH$, is heated with bromine, the lactonic acid,  $COOH\cdot CH<\begin{array}{l}CH(COOH)\\ CMe_2—CO\end{array}>O$, is formed, and this, when fused with caustic potash, yields oxalic and *as*-dimethylsuccinic acids.

M. O. F.

Condensation Products of Cyclic Ketones: Syntheses in the Terpene Series. By Otto Wallach (*Ber.*, 1896, **29**, 2955—2966. Compare Abstr., 1896, i, 572).—The synthetical pulegone, $C_{10}H_{16}O$, obtained by condensation of methylcyclohexenone with acetone (*loc. cit.*), is separated from bye-products by converting it into the *semicarbazone*, which forms two modifications, melting below 100° and at 144°, respectively; the ketone regenerated from these derivatives boils at 94—95° under a pressure of 14 mm., and under atmospheric pressure at 214—215°. The sp. gr. = 0·918, and the refractive index n_D = 1·46732, both at 20°. Representing natural or parapulegone by the formula  $CMe_2:C<\begin{array}{l}CH_2\cdot CH_2\\ CO—CH_2\end{array}>CHMe$, the structure of the synthetical ketone will be either that of pseudopulegone,



$$COMe\cdot CH:C<\begin{array}{l}CH_2—CH_2\\ CH_2\cdot CHMe\end{array}>CH_2,$$

or of orthopulegone,  $CMe_2:C<\begin{array}{l}CO——CH_2\\ CHMe\cdot CH_2\end{array}>CH_2$; the odour of the new ketone is scarcely distinguishable from that of the natural product, but in chemical properties they are widely different.

Pulegol, $C_{10}H_{17}\cdot OH$, is obtained by treating pulegone in ethereal or alcoholic solution with sodium; it is a viscous liquid, having the odour of terpineol, and boils at 103—104° under a pressure of 15 mm., and under atmospheric pressure at 215°. The sp. gr. = 0·912, and the refractive index, n_D = 1·4792 at 20°. When the warm alcohol is treated with phosphoric anhydride, the *terpene*, $C_{10}H_{16}$, is produced; this boils at 173—175°, and at 18° has the sp. gr. = 0·823, and the refractive index n_D = 1·4601. The *benzylidene* compound of synthetical pulegone is a yellowish, friable mass, and melts at 83—84°.

Synthetical pulegone is not the sole product of the action of acetone on methylcyclohexenone. A *compound*, $C_{13}H_{20}O$, is also formed, and the same substance is obtained when mesitylic oxide is employed; it boils at 179—183° in a vacuum.

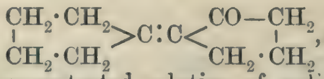
[With Dorrance].—Benzylidenemethylhexenone (*loc. cit.*) condenses with acetone to form the benzylidene compound of synthetical pulegone.

Benzylhexahydrometatoluidine, $CH_2Ph\cdot C_6H_9Me\cdot NH_2$, is obtained by reducing the oxime of benzylidenemethylhexenone (m. p. 109—110°), in alcoholic solution, with sodium; it readily absorbs carbonic anhydride, and boils at 235—245°. The *hydrochloride* is solid, the *carbamide* crystallises in needles and melts at 185°, and the *acetyl* derivative at 168°.

Benzylmethylhexanol (*benzylhexahydrometacresol*),

$$CH_2Ph\cdot C_6H_9Me\cdot OH,$$

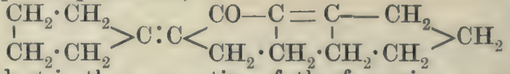
is formed when benzylidenemethylhexenone is reduced in alcoholic solution with sodium; it crystallises from methylic alcohol in beautiful, colourless needles, and melts at 97°. Phosphoric anhydride converts it into *hexahydromethylfluorene*, $C_{14}H_{18}$, which boils at 128° under a pressure of 14 mm.; at 20° it has the sp. gr. = 0·99 and its refractive index $n_D = 1·5455$.

Biscyclopentenepentanone, 

$\begin{matrix}CH_2\cdot CH_2\\ | \\ CH_2\cdot CH_2\end{matrix}\!>C:C<\!\begin{matrix}CO-CH_2\\ | \\ CH_2\cdot CH_2\end{matrix}$

, is obtained by treating pentanone with a concentrated solution of sodium ethoxide; it boils at 117—119° under a pressure of 12 mm., under atmospheric pressure at 253—254°. It has the sp. gr. = 1·0176, and the refractive index $n_D = 1·52095$, both at 20°; the *oxime* melts at 123—124°. The substance is capable of further condensation with benzaldehyde and pentanone under the influence of sodium ethoxide or hydrochloric acid.

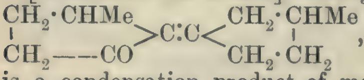
Tricyclodipentenepentanone,



$\begin{matrix}CH_2\cdot CH_2\\ | \\ CH_2\cdot CH_2\end{matrix}\!>C:C<\!\begin{matrix}CO-C=C-CH_2\\ \quad | \quad\; | \\ CH_2\cdot CH_2\cdot CH_2\cdot CH_2\end{matrix}\!>CH_2$

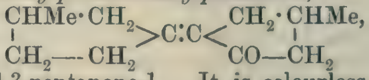
is a bye-product in the preparation of the foregoing compound, and is separated by means of the volatility of the latter in an atmosphere of steam; it crystallises from methylic alcohol in yellowish needles or leaflets, melts at 76—77°, and boils at 190° under a pressure of 12 mm. It does not yield an oxime.

[With Otto M. Ruete].—*Biscyclomethylpentenemethylpentanone*,



$\begin{matrix}CH_2\cdot CHMe\\ | \\ CH_2-\!\!-CO\end{matrix}\!>C:C<\!\begin{matrix}CH_2\cdot CHMe\\ | \\ CH_2\cdot CH_2\end{matrix}$

, or



$\begin{matrix}CHMe\cdot CH_2\\ | \\ CH_2-\!\!-CH_2\end{matrix}\!>C:C<\!\begin{matrix}CH_2\cdot CHMe,\\ | \\ CO-CH_2\end{matrix}$

is a condensation product of methyl-3-pentanone-1. It is colourless and without odour, and boils at 127° under a pressure of 13 mm. The *oxime* melts at 94°, and the *alcohol*, obtained by reduction with sodium, boils at 121° under a pressure of 13 mm.

Biscyclohexenehexanone, $C_{12}H_{18}O$, is obtained from the cyclic hexenone and sodium ethoxide; it is volatile in steam, and forms yellow crystals. The *oxime* melts at 146—148°.

Biscyclomethylhexenemethylhexanone, $C_{14}H_{22}O$, is obtained from methylhexenone and sodium ethoxide, and also by withdrawing the elements of halogen hydride from the compounds $C_{14}H_{23}ClO$, and $C_{14}H_{23}BrO$, produced from methylhexenone and halogen hydride. It boils at 143—144° under a pressure of 10 mm.; its sp. gr. = 0·9635, and its refractive index $n_D = 1·4955$ at 20°. The oxime melts at 152°.

M. O. F.

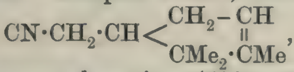
French Oil of Roses. By Justin Dupont and Jacques Guerlain (*Compt. rend.*, 1896, **123**, 700—702).—The authors have made a preliminary examination of two samples of French oil of roses distilled during the years 1895 and 1896. These samples differ considerably from the Bulgarian (Turkish) oil in their general characters, and possess a very much more fragrant smell. The following numbers are given.

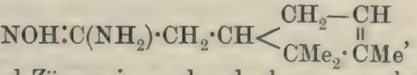
	French, 1895.	French, 1896.	Bulgarian (average).
Sp. gr. 30°/15°	0·8225	0·8407	0·8650
Rotation at 30° (100 mm. tube)	− 6° 45′	− 8° 3′	− 3° 30′
Percentage of stearoptene	35	26	6 to 13

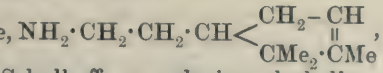
The stearoptene was separated completely from both of the above samples, and melted at 38° in the first case and at 33° in the second.

By a series of fractional crystallisations, two products were obtained from it, the one melting at about 39°, the other at about 24°; this confirms Bertram's statement that *two* solid hydrocarbons exist in rose oil, melting at 20° and 40° respectively, and is opposed to the observations of Markownikoff and Reformatsky (Abstr., 1893, i, 662; comp. also Abstr., 1894, i, 253). The two oils from which the stearoptene had been removed produced rotations of $-10° 30'$ and $-10° 42'$ respectively. The oils were heated for 1 hour with alcoholic potash, and the insoluble portion was separated and fractionated under a pressure of 20 mm. Four fractions were obtained, boiling at 110—120°, 120—125°, 125—150°, and 150—180°. From the first fraction, an optically inactive liquid was obtained boiling at 114—115° (20 mm.), having a sp. gr. = 0·8859, and possessing the odour of geraniol. It is therefore probably geraniol. From the alkaline liquid obtained in the hydrolysis of the oil, a syrupy acid having a powerful and characteristic smell was obtained by acidifying with sulphuric acid and extracting with ether. This will be studied. The above results point to the presence in the French oil of roses of a powerful lævo-rotatory ethereal salt which is hydrolysed on prolonged boiling with water. The hydrolysis of this salt in the preparation of the Turkish oil is thought by the author to account for the diminished fragrance of that oil as compared with the products they have examined, which were obtained by one distillation only.

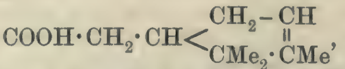
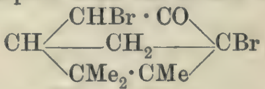
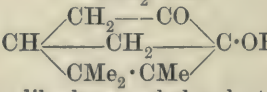
A. C. C.

Camphor. By J. C. W. FERDINAND TIEMANN (*Ber.*, 1896, **29**, 3006—3026. Compare Abstr., 1895, i, 426, 675, 678).—*α*-Campholenonitrile,  $CN\cdot CH_2\cdot CH<\begin{array}{c}CH_2-CH\\ \qquad\|\\ CMe_2\cdot CMe\end{array}$, is most conveniently prepared by heating camphoroxime (500 parts) with 25 per cent. sulphuric acid (1500—2000 parts) in a reflux apparatus for 15 minutes, the source of heat being removed as soon as action commences; it boils at 226—227°, and in a decimetre tube $\alpha = +7·5°$. When hydrogen chloride is passed into an alcoholic solution of the nitrile, *α*-campholenic acid is produced, along with a certain quantity of isoamidocamphor.

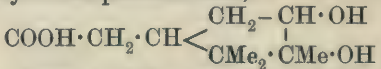
α-Campholenamidoxime,  $NOH\colon C(NH_2)\cdot CH_2\cdot CH<\begin{array}{c}CH_2-CH\\ \qquad\|\\ CMe_2\cdot CMe\end{array}$, first obtained by Goldschmidt and Zürrer, is produced when *α*-campholenonitrile is heated with aqueous hydroxylamine during several days under pressure; it crystallises in white needles melting at 102°, and the hydrochloride melts at 181°.

α-Camphylamine,  $NH_2\cdot CH_2\cdot CH_2\cdot CH<\begin{array}{c}CH_2-CH\\ \qquad\|\\ CMe_2\cdot CMe\end{array}$, was obtained by Goldschmidt and Schulhoff on reducing alcoholic *α*-campholenonitrile with sodium; it boils at 111—112° under a pressure of 25 mm., and at 194—196° under atmospheric pressure. In a decimetre tube, $\alpha = +6°$.

α-Campholenamide (Abstr., 1895, i, 676) crystallises in lustrous leaflets on adding petroleum to the solution in benzene; dissolved in alcohol, it has $[\alpha]_D = -4{\cdot}06°$. Although warm, dilute sulphuric acid converts the amide into the sulphate of isoamidocamphor, incautious treatment with the acid gives rise to dihydrocampholenolactone, with elimination of ammonia.

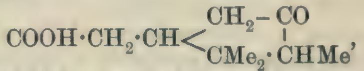
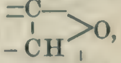
α-Campholenic acid,  $COOH{\cdot}CH_2{\cdot}CH<\begin{matrix}CH_2-CH\\ \Vert\\ CMe_2{\cdot}CMe\end{matrix}$, is obtained on hydrolysing the nitrile or the amide with alcoholic potash, and is identical with the product formed when β-dibromocamphor is heated with dilute alcohol and sodium amalgam. Prepared from this source, it has been known as hydroxycamphor, and its formation from β-dibromocamphor leads the author to regard the latter as having the constitution ; when this is reduced, hydroxycamphor, , is first formed, passing immediately into dihydrocampholenolactone or α-campholenic acid. α-Campholenic acid boils at 256°, and, in a decimetre tube, $\alpha = +9° 37'$, the *calcium* salt crystallises from alcohol in white needles; the ethylic salt boils at 222—224°, and, in a decimetre tube, $\alpha = +10° 20'$.

α-Dihydroxydihydrocampholenic acid,



$$COOH{\cdot}CH_2{\cdot}CH<\begin{matrix}CH_2-CH{\cdot}OH\\ |\\ CMe_2{\cdot}CMe{\cdot}OH\end{matrix}$$

(compare Abstr., 1895, i, 676), was first obtained by Wallach on oxidising crude campholenic acid with potassium permanganate (Abstr., 1892, 1237); it is more conveniently prepared, however, by oxidising an ice-cold solution of sodium α-campholenate with 2 per cent. potassium permanganate, added to the liquid during 2 hours. The acid crystallises from water or chloroform, and melts at 144°; it has $[\alpha]_D = +58{\cdot}03°$.

l-*Pinonic acid*,  $COOH{\cdot}CH_2{\cdot}CH<\begin{matrix}CH_2-CO\\ |\\ CMe_2{\cdot}CHMe\end{matrix}$, is produced along with α-dihydroxydihydrocampholenic acid when α-campholenic acid is oxidised, and is also formed when α-dihydroxydihydrocampholenic acid is submitted to dry distillation, water being eliminated, a change which probably involves the formation of an intermediate product containing the ethylenic oxide group  $\begin{matrix}\equiv C-\\ |\\ -CH\end{matrix}>O$, which undergoes atomic rearrangement into the residue, $\equiv CH{\cdot}CO$. *l*-Pinonic acid separates from water in tetragonal crystals, and melts at 98—99°, forming a colourless, viscous oil, which boils at 178—180° under a pressure of 12 mm.; it has $[\alpha]_D = -21{\cdot}4°$. The *oxime* forms white needles, and melts at 147°, and the *semicarbazone* crystallises from alcohol, and melts at 232°. The acid yields bromoform or carbon tetrabromide under the influence of alkali hypobromite, but the action proceeds with greater difficulty than in the case of inactive pinonic acid; concentrated sulphuric acid converts *l*-pinonic acid into methoethylheptanonolide, and the substance obtained from this source appears to be optically active. In all other properties, *l*-pinonic acid agrees with the inactive substance obtained from pinene.

Isoketocamphoric acid, $COMe{\cdot}CMe_2{\cdot}CH(CH_2{\cdot}COOH)_2$, is obtained alike from α-dihydroxydihydrocampholenic and *l*-pinonic acids by the oxidising action of chromic acid; it separates from ether in large, lustrous crystals, melts at 128—129° (Abstr., 1895, i, 478), and is optically inactive. The *oxime* crystallises in needles, and melts at 185—186°, and the *semicarbazone* at 187°.

Isocamphoronic acid, $COOH{\cdot}CMe_2{\cdot}CH(CH_2{\cdot}COOH)_2$, first obtained by Kachler on oxidising camphor with nitric acid, and subsequently by Kachler and Spitzer on oxidising the mixture of products obtained when β-dibromocamphor is reduced with sodium amalgam, is prepared from α-dihydroxydihydrocampholenic and *l*-pinonic acids by allowing chromic acid to act more vigorously on the substances than is permitted when isoketocamphoric acid is required; in order to separate the acid from terpenylic and terebic acids, it is precipitated with cupric acetate. Isocamphoronic acid melts at 166—167°; its ethylic salt boils at 195—200° under a pressure of 36 mm. According to the above expression, isocamphoronic acid contains a double glutaric acid grouping of the atoms, and, in consequence, yields an anhydride with great difficulty; prolonged treatment with boiling acetic chloride yields an anhydro-acid which dissolves readily in chloroform, and is so rapidly converted into isocamphoronic acid under the influence of water that it has not been found possible to purify it.

The constitution which von Baeyer ascribes to isocamphoronic acid (this vol., i, 82) is not in accordance with this observation; the conversion of the substance into terpenylic acid, which the author has shown to take place under the influence of concentrated sulphuric acid (this vol., i, 91, 158), agrees with the behaviour of α-dimethylglutaric acid when treated with the same agent, γ-isocaprolactone being formed. Moreover, the ready conversion of camphor into carvacrol, paracymene, and metacymene, and, further, the production of trimethylsuccinic acid or its anhydride (1) when camphoronic acid is submitted to dry distillation, (2) on oxidising camphoric acid with chromic acid (3) on heating trimethylpentanonedioic-acid,

$$COOH{\cdot}CHMe{\cdot}CMe_2{\cdot}CO{\cdot}COOH,$$

and (4) by the ultimate oxidation of camphoric acid with potassium permanganate, indicates the presence in the camphor molecule of one carbon atom to which two methyl groups are attached, and a second carbon atom combined with one methyl group; furthermore, these two carbon atoms are united directly with one another, becoming separated when carvacrol or cymene is produced from camphor.

M. O. F.

Crystallographic Properties of Substituted Camphors. By Jules Minguin (*Compt. rend.*, 1896, **122**, 1548—1550).—*Dextrogyrate benzylidenecamphor* forms rhombic prisms of 111° 45′ in which $b = 1000$ and $h = 801{\cdot}6$. The faces observed are $m\ p\ g^3\ a^1\ b^{\frac{1}{2}}\ e^1\ e^2\ e^{\frac{1}{3}}$. The crystals being most commonly formed of $p\ m\ g^3\ b^{\frac{1}{2}}\ a^1\ e^1$. Sometimes e^1 and a^1 are abnormally developed and p and m disappear. No hemihedral faces are observed.

Lævogyrate benzylidenecamphor has precisely the same form and likewise shows no hemihedral faces.

Racemic benzylidenecamphor forms monoclinic prisms of 119° 10′, the inclination of the axes being 25°, whilst $b = 1000$ and $h = 996{\cdot}7$. The general form is $p\ m\ h^1\ b^1\ d^1$, the face p being highly developed.

Anisylidenecamphor forms rhombic prisms of 114° 15′, $b = 1000$ $h = 297{\cdot}4$. The faces observed are $m\ g^1\ g^3\ a^1\ e^1\ e^{\frac{1}{2}}\ b^{\frac{1}{2}}$, $b^{\frac{1}{2}}$ being excessively developed, whilst $a^1\ e^1\ e^{\frac{1}{2}}\ g^1$ are very small.

Methylsalicylidenecamphor.—The ortho-derivative of the preceding (para) compound forms monoclinic prisms of 93° 10′, the inclination being 23° 13′, and $b = 1000$, $h = 852{\cdot}9$. The general form is $p\ m\ g^1\ a^1\ h^1\ e^2$, the face g^1 being very small, whilst h^1 is always strongly developed.

Ethylsalicylidenecamphor forms monoclinic prisms of 103° 8′, the inclination being 26°, and for $b = 1000$, $h = 879{\cdot}6$. The common faces are $p\ m\ g^1\ h^1\ e^1\ b^{\frac{1}{2}}$, and of these $e^1\ g^1\ h^1$ are not always present.

The substitution of more or less complex radicles in the CH_2 group of camphor lowers the symmetry. Amongst those that crystallise in the rhombic system, the angles of the prisms do not greatly differ, and in the zone m there is always an angle of about 160° corresponding with a face g_3. The molecular grouping seems to remain the same, and the ratio of the linear dimensions of the primary form is the most variable element. Racemic benzylidenecamphor and the methyl- and ethyl-salicylidenecamphors differ but little in the zone *ph*, and the angles of inclination of the prisms are nearly the same.

Orthomethylsalicylidenecamphor has less symmetry than the para-isomeride. C. H. B.

Dammar Resin. By G. Glimmann (*Arch. Pharm.*, 1896, **234**, 584—589).—The resin was extracted in a large Soxhlet apparatus with absolute alcohol, and the alcoholic extract was poured into distilled water, whereon a pure white substance separated; a bitter principle remained dissolved in the water. The pure resin separated in this way melts at 100° and dissolves in ether, absolute alcohol, chloroform, benzene, carbon bisulphide, and sulphuric acid; when destructively distilled it yields a product containing phenolic compounds; the ethereal oil obtained by distilling the resin with steam boils at 82°, and smells of pepper.

Dammarolic acid, $OH{\cdot}C_{54}H_{77}O_3(COOH)_2$, is obtained by shaking the ethereal solution of the pure resin with a solution of potash (1 : 1000) and precipitating the acid by hydrochloric acid; it is freely soluble in alcohol, ether, chloroform, benzene, aniline, phenol, sulphuric acid, acetic acid, and carbon bisulphide; light petroleum dissolves it very sparingly. The *copper* and *potassium* salts were analysed, also an *acetyl* and a *benzoyl* derivative, which appear to warrant the above formula for the acid.

The ethereal solution from which the acid has been extracted contains *α-dammar-resen*, $C_{11}H_{17}O$, which melts at 65°, and dissolves in alcohol, ether, chloroform, sulphuric acid, and carbon bisulphide. The portion of the crude resin insoluble in absolute alcohol is only soluble in chloroform, and constitutes *β-dammar-resen*. It melts at 200°. The following is the percentage composition of the dammar resin examined by the author.

Dammarolic acid	23·0
Water	2·5
Ash	3·5
Impurities	8·0
α-Dammar-resen	40·0
β-Dammar-resen	22·5
Loss (ethereal oil, bitter principle)	0·5

A. G. B.

Guaiacum Resin. By OSCAR G. DOEBNER and ED. LÜCKER (*Arch. Pharm.*, 1896, **234**, 590—610).—The following analysis was made by precipitating the alcoholic solution of the resin with alcoholic potash, which throws down potassium guaiaretate, evaporating the filtrate, dissolving the residue in water, precipitating the guaiaconic and guaiacic acids with hydrochloric acid, and separating them by means of ether, in which the former is soluble.

		Per cent.
Soluble in alcohol	Guaiaretic acid	11·15
	Guaiaconic acid	50·00
	Guaiacic acid (β-resin)	11·75
Insoluble in alcohol	Residue *	24·96
	Loss	2·14

* Containing :—

	Per cent.
Ash	2·10
Gum	9·64

Guaiaretic acid was prepared according to the recipe of Hlasiwetz (*Annalen*, 1859, **112**, 182 ; 1861, **119**, 206 ; 1864, **130**, 346). It forms white, lustrous laminæ and melts at 86°. Analyses of the acid are in accord with the formula $C_{20}H_{24}O_4$, not $C_{20}H_{26}O_4$; the *benzoyl* derivative, $C_{20}H_{23}O_4Bz$, forms nearly colourless crystals and melts at 131°. Dry distillation of the acid yields guaiacol, pyroguaiacin, and tiglic aldehyde.

Guaiaconic acid (Hadelich, *J. pr. Chem.*, 1862, **87**, 321) is a white, amorphous powder and melts at 74—76°. Analyses indicate the formula $C_{20}H_{24}O_5$, not $C_{19}H_{20}O_5$, for the acid, and since the acid is insoluble in alkali carbonates it cannot contain a free carboxyl group. The *dibenzoyl* derivative melts at 81—83°, and the *diacetyl* derivative at 61—63°. By destructively distilling the acid, tiglic aldehyde, guaiacol, and pyroguaiacin are obtained, and by fusing it with potash, protocatechuic acid, together with small quantities of volatile fatty acids and phenolic compounds.

Guaiacic acid (Hadelich's β-resin ; *loc. cit.*) was not obtained in a pure condition ; the *benzoyl* derivative, $C_{21}H_{19}Bz_3O_7$, is a white, crystalline powder and melts at 155—158°. By dry distillation of the acid, tiglic aldehyde and creosol were isolated.

"Guaiacum oil" (*guajaköl*) is prepared by boiling guaiacum resin with sodium carbonate solution, filtering from the resin, which separates on cooling, saturating the filtrate with carbonic anhydride, again filtering, and extracting with ether. The oil is left when the

ether is evaporated; it is somewhat freely soluble in water, and freely in alcohol and ether. By acidifying the alkaline solution after it has been extracted with ether, "*guaiacum yellow*," $C_{20}H_{20}O_7$, is precipitated, and may be crystallised in yellow octahedra, which melt at 115° and dissolve in strong sulphuric acid with a cornflower-blue colour.
A. G. B.

Synthesis of the Acids of Guaiacum Resin. By Oscar G. Doebner (*Arch. Pharm.*, 1896, **234**, 610—613).—Tiglic aldehyde (5 parts), guaiacol and creosol (9 parts, comprised of 1 mol. of each) were dissolved in glacial acetic acid, strong hydrochloric acid (2 parts) was added, and the mixture heated for 20 minutes on the water bath; the liquid was then poured into strong hydrochloric acid (250 c.c.), heated for 15 minutes, and finally poured into cold water. The brown resin which separated has the formula $C_{20}H_{24}O_4$, and is therefore isomeric with guaiaretic acid (see preceding abstract); from its formation, the constitution

$$CHMe\!:\!CMe\cdot CH[C_6H_2Me(OMe)(OH)]\cdot C_6H_3(OMe)\cdot OH$$

may be ascribed to it. It is insoluble in water, soluble in alcohol, and dissolves in strong sulphuric acid with a cherry-red colour.

A similar resin, of the empirical formula of guaiaconic acid, was obtained by the condensation of tiglic aldehyde with a mixture of guaiacol (1 mol.) and pyrogallol dimethyl ether (1 mol.). It does not give a blue coloration with oxidising agents.

Finally, a resin, $C_{21}H_{26}O_6$, has been prepared from pyrogallol dimethyl ether (2 mols.) and tiglic aldehyde, which dissolves in strong sulphuric acid with a red colour.

The view that certain resins may be regarded as condensation products of aldehydes with phenols is upheld by these experiments.
A. G. B.

Guaiacum Blue. By Oscar G. Doebner (*Arch. Pharm.*, 1896, **234**, 614—620).—After enumerating the oxidising agents which are capable of producing guaiacum blue, the author points out that the colouring matter is an oxidation product of guaiaconic acid, and is best prepared by shaking 100 c.c. of a solution of this acid (10 grams) in 96 per cent. alcohol (1 litre) with a solution of ferric chloride (10 grams) in water (3 litres). The blue flocks which separate are rapidly filtered off, washed with cold water, and dried over calcium chloride in a vacuum protected from light. By subsequently washing with benzene, any unaltered guaiaconic acid may be removed. The blue powder thus prepared has the formula $C_{20}H_{20}O_6$ or $C_{20}H_{22}O_6$, the former being more in accord with its formation from guaiaconic acid than the latter is. It appears that the colour of the blue compound is dependent on the oxygen which it contains in excess of that in the parent guaiaconic acid, this oxygen being in much the same condition as that in which the second atom of oxygen exists in hydrogen peroxide; thus, a number of oxidising agents will bleach the colouring matter, themselves suffering reduction. The blue loses oxygen and is bleached at 100°. Its solutions in glacial acetic acid and in alcohol are deep blue, but they very rapidly lose oxygen, becoming colourless. This oxygen is probably not eliminated in the form of ozone, since, when it is set free by a dilute acid, it does not liberate iodine from potassium iodide; this is also the case with the oxygen liberated from hydrogen peroxide by a dilute acid.

Regarding guaiaconic acid as consisting of a condensation product of tiglic aldehyde, guaiacol, and pyrogallol dimethyl ether, the author constructs a formula for the blue which is built on the lines of that for cœrulignone, the oxidation product of pyrogallol dimethyl ether.

In the well-known tests which depend on the formation of guaiacum blue, it is better to use guaiaconic acid itself than to use guaiacum.

A. G. B.

The Action of Formaldehyde on Aloïn. By C. Emanuel Merck (*Chem. Centr.*, 1896, i, 561; from *Ber. ü. d. Jahr.*, 1895, 21—23).—By the action of formaldehyde and concentrated sulphuric acid on aloïn, a condensation product, $CH_2\!:\!C_{17}H_{16}O_7$, is obtained as an amorphous, tasteless powder, which, on heating above 260°, becomes black. It dissolves in dilute sodium hydroxide solution, forming a yellow solution, from which it is reprecipitated by acids. It forms a yellow solution in concentrated sulphuric acid, and a reddish-yellow solution in concentrated nitric acid.

E. W. W.

Bitter Principles contained in the Leaves of Leucodendron concinnum. By C. Emanuel Merck (*Chem. Centr.*, 1896, i, 561; from *Ber. ü. d. Jahr.*, 1895, 3—7).—From the leaves of this plant, which is native to the Cape and of the order of *Proteaceæ*, a glucoside *leucoglycodrin*, $C_{27}H_{42}O_{10}$ or $C_{27}H_{44}O_{10}$, may be obtained as a bitter, white powder, by evaporating the alcoholic extract and repeatedly dissolving the residue in alcohol and precipitating with ether. It has a specific rotatory power $[\alpha]_D = -40{\cdot}25°$ and is decomposed by water. By the action of 2 per cent. sulphuric acid at 100°, a brown oil is produced, which, when treated with acetic anhydride, yields white crystals and an almost colourless liquid. From this liquid, which reduces Fehling's solution, a phenylglucosazone melting at 181—192° can be obtained (δ-galactose or glucose?).

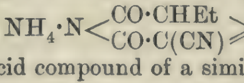
By further evaporation of the alcoholic extract, a second bitter principle, *leucodrin*, may be isolated, which is possibly identical with proteacin, obtained by Meiring Beck from the same plant. Leucodrin, $C_{15}H_{16}O_8$, has a specific rotatory power, $[\alpha]_D = -15{\cdot}45°$, and crystallises in white prisms which are very sparingly soluble in water, and only slightly so in cold alcohol. *Octacetylleucodrin*, $C_{15}H_8O_8Ac_8$, which melts at 188—190°, is formed by the action of acetic anhydride on leucodrin. (Compare Hesse, Abstr., 1896, i, 495).

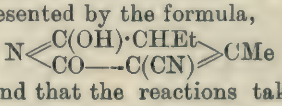
E. W. W.

A Crystalline Bitter Principle contained in Plumiera acutifolia. By C. Emanuel Merck (*Chem. Centr.*, 1896, i, 561; from *Ber. ü. d. Jahr.*, 1895, 11—13).—This substance, $C_{57}H_{72}O_{33} + 2H_2O$, obtained by evaporation of the alcoholic extract, melts at 157—158° and forms a colourless solution in concentrated sulphuric acid, which, on warming, turns yellow, reddish-yellow, brownish-red, or black. Its solution in concentrated nitric acid is also colourless, but becomes yellow on warming, and, similarly, the solution in sodium hydroxide turns yellow on boiling. This substance cannot be identical with plumieride, which has beeen isolated by Boorsma.

E. W. W.

Compounds contained in Radix imperatoriae ostruthium. By C. EMANUEL MERCK (*Chem. Centr.*, 1896, i, 561; from *Ber. ü. d. Jahr.*, 1895, 8—10).—In the taproot of this plant three substances have already been found, namely, peucedanin, oxypeucedanin, which the author regards as a homogeneous compound in opposition to the views of Hlasiwetz and Weidel, and ostruthin. The author has obtained a new substance *osthin* $C_{15}H_{16}O_5$ which crystallises from dilute alcohol in slender, yellow needles, melts at 199—200°, and is insoluble in water. In concentrated sulphuric acid, it forms a yellow solution, which, on warming, becomes dark red. Its solutions in alkalis and ammonia are also yellow. *Diacetylosthin*, $C_{15}H_{14}O_5Ac_2$ melts at 183—186°. *Monoacetylosthin* melts at about 171—180°. In the original paper, a table of the melting points, solubilities, &c., of these four plant substances is given. E. W. W.

Synthesis of Pyridine Compounds from Ethereal Salts of Ketonic Acids and Ethylic Cyanacetate in Presence of Ammonia or Amines. By ICILIO GUARESCHI (*Chem. Centr.*, 1896, i, 601—603; from *Estr. Mem. Reale Accad. Sci. Torino*, ii, 46).—By the action of ammonia on homologues of ethylic acetoacetate, an ethereal salt of an amido-acid, $NH_2\cdot CMe\colon CMe\cdot COOEt$, and an amide of a β-ketonic acid, $COMe\cdot CHMe\cdot CO\cdot NH_2$, are formed. But in the presence of ammonia, or an amine, the cyanacetamide first produced reacts with the β-ketonic acid amide to form a pyridine derivative, the condensation taking place with ease at the ordinary temperature. In this way, ethylacetoacetamide and ethylic cyanacetate form an ammonium salt,  $NH_4\cdot N\left\langle\begin{matrix}CO\cdot CHEt\\ CO\cdot C(CN)\end{matrix}\right\rangle CMe$, from which hydrochloric acid liberates an acid compound of a similar constitution, or more probably possessing a composition represented by the formula,



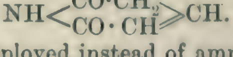
$$N\left\langle\begin{matrix}C(OH)\cdot CHEt\\ CO—C(CN)\end{matrix}\right\rangle CMe \quad (I).$$

The author has found that the reactions take place directly between cyanacetamide and β-ketonic acid amides or ethereal salts of ketonic acids, and similarly also between ketonic acid amides and ethylic cyanacetate. The new compounds thus formed have acid properties, yield dyes and, with ferric chloride, give a bluish-violet coloration or precipitate. Those derived from ethylic acetoacetate, and containing the group $-CH_2\cdot C(OH)=$, form precipitates with copper sulphate and acetate, and become coloured by the action of potassium nitrite or of bromine water, whilst those containing the substituted group,

$$-CHMe\cdot C(OH)=,$$

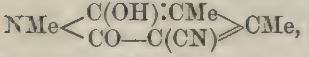
do not give these reactions.

To all these new substances, the author gives formulæ analogous to (I), representing them as αβ′-dihydropyridine derivatives, and regarding them also as derived from glutaconimide,



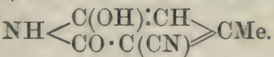
$$NH\left\langle\begin{matrix}CO\cdot CH_2\\ CO\cdot CH\end{matrix}\right\rangle CH.$$

When an amine is employed instead of ammonia, the resulting compounds contain an alkyl group directly united to nitrogen, and as these also have acid properties, this acidity cannot be ascribed to the presence of an imide group, but the presence of a hydroxyl group must be assumed as in the formula, $\mathrm{NMe}{<}\substack{\mathrm{C(OH){:}CH}\\ \mathrm{CO\cdot C(CN)}}{>}\mathrm{CMe}$ (II). Similarly, the compound obtained from methylamine and ethylic methylacetoacetate is to be regarded as containing a hydroxyl group, since it forms a silver compound, and with ferric chloride gives a coloration, although this is very fugitive. Its formula is therefore written,



$$\mathrm{NMe}{<}\substack{\mathrm{C(OH){:}CMe}\\ \mathrm{CO{-}C(CN)}}{>}\mathrm{CMe}, \text{ (III).}$$

The constitution of the compounds which do not contain substituted imide groups the author prefers, for the present, to write in accordance with the formula (II) rather than with the formula



$$\mathrm{NH}{<}\substack{\mathrm{C(OH){:}CH}\\ \mathrm{CO\cdot C(CN)}}{>}\mathrm{CMe}.$$

3-*Cyano*-6-*hydroxy*-4-*methyl*-5-*ethyl*-$\Delta^{3,6}$-*dihydropyridone* (Formula (I)), prepared from ethylacetoacetamide, ammonia, and ethylic cyanacetate, melts at 234—235°, and is slightly soluble in cold water. The ammonium and the copper salts, $(C_9H_9N_2O_2)_2Cu$ and $C_9H_8CuN_2O_2$, have been analysed, and the sodium and magnesium salts prepared.

3-*Cyano*-6-*hydroxy*-4-*methyl*-$\Delta^{3,6}$-*dihydropyridone* or *cyanomethylglutaconimide*, $\mathrm{N}{<}\substack{\mathrm{C(OH)\cdot CH_2}\\ \mathrm{CO{-}C(CN)}}{>}\mathrm{CMe}$, is obtained by the action of ethylic acetoacetate, ammonia, and ethylic cyanacetate; at 295°, it becomes brown, and is charred at 300—304°; it yields a bromine derivative, which is decomposed by water or alcohol. By means of this reaction, the author proved that acetoacetamide is formed by the action of ammonia on ethylic acetoacetate. The ammonium, sodium, barium, silver, copper, and copper ammonium salts were analysed. The author was unable to determine whether the cyanodihydropyridinecarboxylic acid prepared by Held from ammonia and ethylic cyanacetate is identical with this compound.

3-*Cyano*-6-*hydroxy*-1-*methyl*-$\Delta^{3,5}$-*dihydropyridone* or *cyanomethylglutaconmethylimide* (Formula (II)), prepared from ethylic acetoacetate, methylamine, and ethylic cyanacetate, melts at about 285°, and its silver salt was analysed. The 1-*ethyl* compound or *cyanomethylglutaconethylimide*, which melts at about 242°, and the 1-allyl compound or *cyanomethylglutaconallylimide*, which melts at 222°, may be obtained by similar reactions.

3-*Cyano*-6-*hydroxy*-4-*methyl*-5-*ethyl*-$\Delta^{3,6}$-1-*dihydropyridone*, or *methylcyanomethylglutaconimide*, prepared from methylacetoacetamide, ammonia, and ethylic cyanacetate, melts at 270—272°. The ammonium, sodium, silver, barium, and copper salts were analysed. 3-*Cyano*-6-*hydroxy*-1 : 4 : 5-*trimethyl*-$\Delta^{3,5}$-*dihydropyridone* (Formula (III)), prepared from ethylic methylacetoacetate, methylamine, and ethylic cyanacetate, melts at 264—265°. With ferric chloride, it first gives a coloration, and is then oxidised to a compound which melts at 235°. *Amidobenzoylacetamide*, $\mathrm{NH_2\cdot CPh{:}CH\cdot CO\cdot NH_2}$, which melts at 164—165°, and *cyanophenylglutaconimide*, which melts at 280—282°, are obtained by the interaction of ethylic benzoylacetate, ammonia, and ethylic cyanacetate.

E. W. W.

Stereochemistry in the Piperidine Series. By CARL D. HARRIES (*Ber.*, 1896, **29**, 2730—2731).—It has been already stated that vinyldiacetonamidoxime, on reduction with zinc and alcoholic hydrochloric acid, yields paramidotrimethylpiperidine. Further investigation showed that this oxime, on treatment with sodium and boiling amylic alcohol. was reduced to an isomeric paramidotrimethylpiperidine, the two amines being easily identified by means of their hydrochlorides, that of the former being generally oily, whilst that of the latter is a fine, crystalline solid. On treating the two bases with nitric acid, two hydroxyalkylamines (hydroxytrimethylpiperidines) are produced, the first being the compound (m. p. 123°) obtained by E. Fisher from vinyldiacetonamine by direct reduction, the second a compound melting at 160—161°. Both these compounds are also produced by the reduction of vinyldiacetonamine (oxytrimethyltetrahydropyridine) with sodium amalgam, and can be separated by fractional crystallisation. The former (m. p. 123°) is, however, not a homogeneous substance, but is a mixture of the base melting at 160—161°, with a new hydroxytrimethylpiperidine melting at 137—138°, the two being easily separated by means of their hydrochlorides. Both the compound melting at 160—161°, and the mixture (m. p. 123°) pass, on treatment with sodium amyloxide, into the stable compound melting at 137—138°. This subject will be treated more fully in a paper to be published in the *Annalen.* J. F. T.

Diphenylindone. By ADOLF DAHL (*Ber.*, 1896, **29**, 2839—2842. Compare Abstr., 1896, i, 146).—When diphenylindone is heated with hydriodic acid and phosphorus during 6 hours at 150—160°, *triphenylpropane*, $CHPh_2\cdot CHMePh$, is produced. It distils unaltered at 365°, solidifying to a hard, white mass; no crystalline derivative could be obtained.

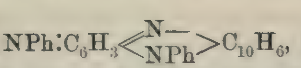
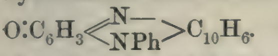
Triphenyllactic acid is formed when diphenylindone is fused with potash at a moderate temperature. It crystallises from glacial acetic acid in yellowish crystals resembling those of common salt, and melts at 189°. Its constitution has not yet been definitely ascertained.

Methylic triphenylacrylate occurs in the bye-products obtained in the preparation of diphenylindone (*loc. cit.*). It crystallises from light petroleum in yellow needles, melting at 136°, and yields triphenylacrylic acid on hydrolysis. A. L.

Quinolineoxyquinolines. By PAUL COHN (*Monatsh.*, 1896, **17**, 667—671).—When 2′-chloroquinoline is heated with excess of 1-hydroxyquinoline, a reaction takes place, the evolution of hydrogen chloride being violent at 165°. The product, $C_9NH_6\cdot O\cdot C_9NH_6$, crystallises in yellow needles, and melts at 175° (uncorr.). The yellowish *hydrochloride*, $C_{18}H_{12}N_2O,HCl$, which is decomposed by water, the yellow *platinochloride*, $C_{18}H_{12}N_2O,H_2PtCl_6$, and the brownish-yellow *palladiochloride*, $C_{18}H_{12}N_2O,H_2PdCl_4 + H_2O$, were also prepared.

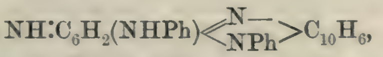
2′-Chloroquinoline also reacts with 3-hydroxyquinoline, but less readily. The product, isomeric with that described above, crystallises in yellowish needles, and melts at 120°; the yellow *platinochloride*, $C_{18}H_{12}N_2O,H_2PtCl_6$, was also prepared and analysed. C. F. B.

The Isorosindulines. By OTTO FISCHER and EDUARD HEPP (*Ber.*, 1896, **29**, 2752—2760).—The authors propose to retain the name isorosinduline in the sense in which they have previously (*Annalen*, **272**, 306) employed it, and to apply the term pseudorosinduline to the compounds called isorosindulines by Kehrmann (*Annalen*, **290**, 247). They have examined the isorosinduline prepared by Nietzki and Otto (Abstr., 1888, 843) from quinonedichlorodiimide and phenyl-β-naphthylamine, in order to ascertain in what respects it is analogous to the safranines.

Phenylisorosinduline,  $\mathrm{NPh{:}C_6H_3}<\substack{\mathrm{N}-\\ \mathrm{NPh}}>\mathrm{C_{10}H_6}$, is prepared by the action of nitrosodiphenylamine on β-naphthylphenylamine. The *hydrochloride* crystallises in long, flat prisms with a copper-red lustre. The *nitrate* crystallises well in thick prisms, which have a metallic lustre. The base also forms crystals, which have a coppery lustre. It melts at 169—171°, and imparts a blue colour to sulphuric acid. Concentrated hydrochloric acid at 230—240° converts the base into *isorosindone*,  $\mathrm{O{:}C_6H_3}<\substack{\mathrm{N}-\\ \mathrm{NPh}}>\mathrm{C_{10}H_6}$. This substance is best prepared from nitrosophenol and β-naphthylphenylamine, and is a weak base, the *hydrochloride* of which dissociates in aqueous solution. The free base crystallises in prisms, which have a dark bronze lustre, and melt at 223—224°. With ferric chloride, the hydrochloride forms a characteristic *double salt*, crystallising in golden yellow needles.

Hydroxyisorosindone, $\mathrm{O{:}C_6H_7(OH)}<\substack{\mathrm{N}-\\ \mathrm{NPh}}>\mathrm{C_{10}H_6}$, is formed when isorosindone is boiled with concentrated alcoholic potash; it crystallises in red needles, which have a bronze lustre. The *potassium salt* is readily soluble in water, sparingly in potash.

Methoxyisorosindone crystallises in needles, which melt at 274°, and have a greenish lustre.

Anilidoisorosinduline,  $\mathrm{NH{:}C_6H_2(NHPh)}<\substack{\mathrm{N}-\\ \mathrm{NPh}}>\mathrm{C_{10}H_6}$, is obtained by the action of aniline and its hydrochloride on isorosinduline in alcoholic solution. The *hydrochloride* crystallises in prisms, with a greenish lustre. The free base forms brownish-red needles, which have a bluish lustre and melt at 151—152°. *Phenylanilidoisorosinduline* is formed when isorosinduline is heated at 150—160° with aniline and aniline hydrochloride, and crystallises with 1 molecule of benzene in needles which have a dark bronze lustre. *Anilidoisorosindone* is formed when anilidoisorosinduline is heated with hydrochloric acid at 160—170°; it crystallises in lustrous needles, with a bronze lustre.

Ethylisorosinduline, $\mathrm{NH{:}C_6H_3}<\substack{\mathrm{N}-\\ \mathrm{NEt}}>\mathrm{C_{10}H_6}$, is obtained by the reaction of quinonedichlorodiimide and β-naphthylethylamine. The *hydrochloride* forms short, flat, red prisms; the *nitrate* is less soluble than the hydrochloride, and crystallises in dark needles, which have a bronze lustre.

Ethylisorosindone forms slender, brownish-red needles, and melts at 178°; the *hydrochloride* crystallises in dark brown prisms.

Isorosinduline is converted by the action of nitrous acid into a diazo-compound. When this solution is treated with alcohol, nitrogen is evolved, and phenylnaphthophenazonium chloride is produced identical with the substance formed when rosinduline itself is treated in a similar manner. When the diazo-solution is treated with alcohol, and then, after a time, with a large excess of ammonia, rosinduline is formed, so that by this reaction the isorosinduline can be converted into rosinduline. A. H.

Azonium Compounds from Aposafranine, Rosinduline, and their Isomerides. By FRIEDRICH KEHRMANN and W. SCHAPOSCHNIKOFF (*Ber.*, 1896, **29**, 2967—2972. Compare this vol., i, 107.)—In consequence of Fischer and Hepp's publication (preceding abstract), the authors describe the following compounds which they have prepared.

An additive compound of phenylphenazonium chloride and ferric chloride, $C_{18}H_{13}N_2Cl,FeCl_3$, was prepared by the method previously described. If prepared from pure aposafranine, it crystallises readily from its acetic acid solution, otherwise a black, tarry mass is obtained; the crystals are light reddish-brown, thick needles, and melt at 186°. It is readily soluble in water, and in boiling alcohol and acetic acid, but practically insoluble in a saturated ferric chloride solution, in 20 per cent. hydrochloric acid, and in ether.

Phenylphenazonium nitrate, $C_{18}H_{13}N_2{\cdot}NO_3$, was prepared from a cold, aqueous solution of the ferric chloride compound; this was rendered slightly alkaline by adding cold, dilute ammonium carbonate solution drop by drop, filtered into a few drops of dilute nitric acid, and then saturated with pure sodium nitrate. After the lapse of several days, the nitrate separated in reddish-brown crystals. It crystallises from alcohol in thick cubes, melts at 192°, and is readily soluble in water and alcohol.

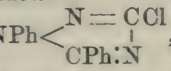
Phenylnaphthophenazonium chloride forms an additive compound with ferric chloride, which can be obtained by deamidating either rosinduline or Nietzki and Otto's isorosinduline, and has already been described.

Phenylnaphthophenazonium nitrate, $C_{22}H_{15}N_2{\cdot}NO_3$, recrystallised from alcohol, forms orange-yellow plates, melts at 225°, and is moderately soluble in cold water.

Phenylnaphthophenazonium platinochloride $(C_{22}H_{15}N_2)_2PtCl_6$, is a brick-red, crystalline powder, practically insoluble in water.

Phenylnaphthophenazonium dichromate, $(C_{22}H_{15}N_2)_2Cr_2O_7$, is also a red, crystalline powder which is insoluble in water. The *iodide*, $C_{22}H_{15}N_2I$, crystallises from alcohol in black plates. J. J. S.

Some Phenyltriazoles. By ASTRID CLEVE (*Ber.*, 1896, **29**, 2671—2677).—This paper has been published earlier than was originally intended on account of the work done on the same subject by Young (Trans., 1895, 1063). The oxytriazoles that Widman has prepared (Abstr., 1896, i, 629) by treating α-acidylphenylsemicarbazides with dilute alkaline hydroxides, were converted into chlorotriazoles by heating them for 3—5 hours at 150° in a sealed tube with the calculated quantity of phosphoric chloride, together with a little phosphorus oxychloride. The chlorotriazoles were then reduced to triazoles by heating them for about 3 hours at 150—160° in a sealed tube with excess of concentrated hydriodic acid (sp. gr. 1·7)and a little red phosphorus. The triazoles are weak bases; the chlorotriazoles, on the other hand, seldom form hydrochlorides.

3-*Chloro*-1:5-*diphenyl*-1:2:4-*triazole*,  $\mathrm{NPh}\left\langle\begin{matrix}\mathrm{N{=}CCl}\\ \vert \\ \mathrm{CPh{:}N}\end{matrix}\right.$, melts at 96°; the reddish-yellow *platinochloride* decomposes at 195°. 1:5-Diphenyltriazole melts at 91°, its yellowish-white *picrate* at 139°; the platinochloride crystallises with $4H_2O$ (and also with $3H_2O + 2HCl$?). 3:1:5-*Methoxydiphenyltriazole* was prepared by treating the hydroxytriazole in alcoholic solution with sodium methoxide and methylic iodide; it melts at 88°, and has basic properties. 3-*Chloro*-1-*phenyl*-5-*isopropyltriazole* melts at 56°, the *triazole* itself at 58°. 3-*Chloro*-1-*phenyl*-5-*propyltriazole* and the corresponding *triazole* were obtained as oils; the yellowish-white *picrate* of the latter melts at 128—130°, and the *platinochloride* crystallises with $4H_2O$. 3-*Chloro*-5-*butylphenyltriazole* and the corresponding triazole are also oils.

C. F. B.

Asymmetric Nitrogen (IV.) Isoconiine. By ALBERT LADENBURG (*Ber.*, 1896, **29**, 2706—2709).—The existence of isconiine having been called in question, the author now brings forward a series of experiments, showing that it is in reality a homogeneous substance, and not a mixture of *d*- and *r*-coniine.

The platinochloride of the compounds, produced by the distillation of *d*-coniine hydrochloride with zinc dust, behaves differently from the platinochloride of a mixture of *d*- and *r*-coniine; in the former case, a crystalline residue remains after treatment with a mixture of alcohol and ether, whilst in the latter the platinochloride entirely dissolves. This insoluble residue, which is the platinochloride of isoconiine, must therefore be free from *d*- and *r*-coniine.

Similarly, the rotation of benzoylisoconiine is very different from that of the benzoyl compound of a mixture of *d*- and *r*-coniine.

Finally, no pure *d*-coniine (rotatory power 18·3°) could be isolated from isoconiine, which would be the case were it a mixture of *d*- and *r*-coniine.

J. F. T.

Tropinic Acid. By GIACOMO L. CIAMICIAN and PAUL G. SILBER (*Ber.*, 1896, **29**, 2975—2976. Compare Abstr., 1896, i, 513).—The authors state that the aurochloride of the base, previously described by them as obtained by the action of hydriodic acid and phosphorus on tropinic acid, has proved not to be identical with *a*-methylpyrolidine aurochloride, as was at first thought possible. The base is probably a trialkylamine, obtained by the complete decomposition of the tropinic acid molecule.

J. J. S.

Attempts to Determine the Constitution of Tropanine and Granatanine Bases by Cryoscopic Methods. By FELICE GARELLI (*Ber.*, 1896, **29**, 2972—2975. Compare Abstr., 1894, i, 157; 1895, ii, 205).—The author has previously shown that similarly-constituted substances can form solutions, which, on cooling, yield abnormal results for the depression of the freezing point. This phenomenon can be made use of in solving questions as to the constitution of different compounds. As regards tropanine and granatanine, the author is able to show that their cryoscopic behaviour agrees with the constitutions already deduced from chemical considerations. Both are to be regarded as containing two nuclei, like naphthalene, the two rings, however, being joined respectively in the para- and meta-positions in the two compounds.

Normal freezing point depressions were obtained with the two compounds in benzene and also in diphenyl solutions, but abnormal results in naphthalene solutions. Special precautions were taken on account of the readiness with which the bases combine with water and carbonic anhydride. J. J. S.

Alkaloids contained in the Seeds of Blue and White Lupines. By Shermann Davis (*Chem. Centr.*, 1896, i, 708—709; from *Apoth. Zeit.*, 11, 94—95).—A comparison of the alkaloids obtained from the seeds of *Lupinus angustifolius* and *L. albus*, respectively, led to the following conclusions. The composition of these compounds or *lupanines* is represented by the formula, $C_{15}H_{24}N_2O$, ascribed to them by Siebert (Abstr., 1892, 223), and by Soldaini (Abstr., 1896, i, 193). The lupanine from *L. albus* described by Soldaini as deliquescent is identical with the liquid lupanine from the same plant, and also with the liquid alkaloid obtained by Siebert from *L. angustifolius*. The identity of these compounds was proved by comparison of numerous salts, both chemically and crystallographically. This alkaloid, which the author names *dextrolupanine*, can in reality be readily obtained in a crystalline form, separating from light petroleum in colourless needles, which melt at 44°, and whose aqueous solution is dextrorotatory.

Soldaini's solid lupanine from *L. albus*, which melts at 99° and is optically inactive, has a composition represented by the formula $C_{15}H_{24}N_2O$, or $C_{30}H_{48}N_4O_2$. By converting it into thiocyanate, it may be separated into two components, dextro- and lævo-lupanine respectively. The free bases obtained from these salts form colourless needles which melt at 44°, and re-form the original inactive lupanine when mixed in equal parts. The dextro-component is identical with the dextro-lupanine obtained from blue and white lupines. None of the groups OH, OMe, CO, or COH, is present in lupanines. By the action of bromine on dextrolupanine hydrochloride in alcoholic solution, two new bases, $C_8H_{15}NO$ and $C_7H_{11}NO$, are obtained, each of which contains a hydroxyl group. The constitution of lupanine is, therefore, probably represented by the formula $C_8H_{15}N \cdot O \cdot C_7H_{11}N$.

E. W. W.

The Alkaloids of Corydalis. (By Ernst A. Schmidt (*Arch. Pharm.*, 1896, 234, 489—491. Compare the following abstract).—Corydaline and corybulbine behave towards iodine in a similar manner to canadine (Abstr., 1894, i, 479). The details of the experiments are given in the following abstract. A. H.

The Alkaloids of Corydalis Cava. By H. ZIEGENBEIN (*Arch. Pharm.*, 1896, **234**, 482—537. Compare the preceding abstract).—The alkaloids were obtained from *Corydalis cava* by the method described by Freund and Josephi (Abstr., 1894, i, 100). The author finds that the formula of corydaline is most probably $C_{22}H_{27}NO_4$, in agreement with Freund and Josephi, whereas Dobbie and Lauder (Trans., 1892, 605) have proposed the formula $C_{22}H_{29}NO_4$. The hydrochloride could not be obtained crystalline. The hydrobromide and hydriodide are white when pure, but become yellow when exposed to the air. The *nitrate* crystallises in lustrous tablets melting at 198°. The *aurochloride*, $(C_{22}H_{27}NO_4,HCl)_2,AuCl_3$, crystallises in very characteristic rosettes of needles melting at 207°. A compound of the normal formula could not be obtained. Hemipinic acid was obtained by the oxidation of the alkaloid, the result previously published by Dobbie and Lauder (Trans., 1894, 57) being thus confirmed.

When corydaline is treated with iodine and alcohol, it is converted into *dehydrocorydaline hydriodide*, $C_{22}H_{23}NO_4,HI$, 4 atoms of hydrogen being removed from the molecule. This substance crystallises with $2H_2O$ and forms lustrous, pale yellow needles. The corresponding *hydrochloride*, $C_{22}H_{23}NO_4,HCl + 4H_2O$, crystallises in yellow plates and prisms. The *aurochloride* has the normal formula and melts at 219°. The *platinochloride* crystallises in long needles containing $6H_2O$. The *hydrobromide* crystallises in yellowish-brown needles, and softens at 126°, melting at a slightly higher temperature. The *hydrogen sulphate* separates from hot water in yellow, prismatic crystals. The *nitrate* crystallises in yellow needles.

When the hydriodide is treated with chloroform and caustic soda, an additive compound, $C_{22}H_{23}NO_4,CHCl_3$, is formed, which crystallises from chloroform in almost colourless tablets, melts at 162—163°, and does not lose weight at 100°. A compound with acetone was prepared in a similar manner but could not be obtained crystalline. This substance serves as a convenient source for the salts of the base, since it is readily decomposed by dilute acids, acetone and the corresponding salt of the base being produced. Dehydrocorydaline also appears to form a hydropolysulphide when its hydriodide is treated with yellow ammonium sulphide. The free base has been obtained in yellow crystals but only in extremely small quantity. When dehydrocorydaline is reduced, it is converted into a base which has the composition and melting point of corydaline and also gives many of the same reactions; it, however, forms a normal *aurochloride*,

$$C_{22}H_{27}NO_4,HAuCl_4 + 4H_2O,$$

which crystallises in slender, pale yellow prisms. Dehydrocorydaline, like corydaline itself, contains four methoxy-groups, and therefore has the formula $C_{18}H_{11}N(OMe)_4$.

Bulbocapnine is not acted on by iodine in a similar manner to corydaline. The methiodide melts at 235—240°, whereas Freund and Josephi give the melting point 257°. When treated with acetic anhydride, the alkaloid is converted into the *triacetyl* derivative,

$$C_{18}H_{13}N(OMe)(OAc)_3,$$

which crystallises in white needles and yields a crystalline *hydrochloride* and *platinochloride* which appear to have abnormal compositions.

Corycavine melts at 216—217° (214—215°, Freund and Josephi). It appears to have the formula $C_{23}H_{23}NO_6$, and not $C_{23}H_{23}NO_5$ as stated by Freund and Josephi; this also agrees with the composition of its salts. The *hydrochloride*, $C_{23}H_{23}NO_6,HCl$, crystallises in compact needles and the *platinochloride*, $(C_{23}H_{23}NO_6)_2,H_2PtCl_6 + 3H_2O$, in pale yellow granules. The alkaloid does not appear to be affected by iodine.

Corybulbine, $C_{21}H_{25}NO_4$, melts at 238—240°. The *hydrochloride* crystallises in yellowish prisms, and the *platinochloride* crystallises with $3H_2O$. Iodine acts on the base as it does on corydaline, but the product has not been obtained in sufficient quantity for analysis.

A. H.

Erythrophleïne. By Erich Harnack (*Arch. Pharm.*, 1896, **234**, 561—570).—The author has recently examined a sample of "*Erythrophleïn hydrochloricum*" prepared by E. Merck, which yields a base differing in several important points from that previously investigated (Harnack and Zabrocki, *Arch. exper. Path. Pharm.*, **15**). The question whether the alkaloid was in each case obtained from a parent bark of the same species (*Erythrophleum guineense*) remains unsettled.

The commercial hydrochloride is a fine, bright yellow, amorphous powder which is hygroscopic, and gradually agglomerates to a dry, solid mass when kept; it dissolves freely in cold water, and the solution has a tendency to froth. The base itself is precipitated by alkalis from the solution of the hydrochloride; it is freely soluble in alcohol and ether, soluble in amylic alcohol and ethylic acetate, and insoluble in light petroleum; its crystallisation has not been accomplished. The *platinochloride* and the *bismuthoiodide* are described and were analysed, but a decision could not be made between the formulæ $C_{28}H_{43}NO_7$ and $C_{28}H_{45}NO_7$ for the base.

When the hydrochloride of the base is heated with hydrochloric acid (38 per cent.) in a reflux apparatus, it undergoes hydrolysis, forming *erythrophleic acid*, $C_{27}H_{40}O_8$ or $C_{27}H_{42}O_8$, and methylamine; the acid is not decidedly crystalline. A. G. B.

Serum-albumin Crystals. By A. Michel (*Chem. Centr.*, 1896, i, 757—758, from *Verh. physiol. med. Ges. Würzburg*, **29**, No. 3, and *Centr. med. Wiss.*, 1896, 152—153).—The crystals were prepared from horse's blood serum. An equal volume of saturated solution of ammonium sulphate is added to the serum, and the globulin which is thus precipitated is filtered off. To the filtrate, ammonium sulphate solution is added until it just gets cloudy. The crystals of albumin sink, and are purified by repeatedly dissolving them in water and precipitating by ammonium sulphate; they are doubly-refracting, hexagonal prisms about a centimetre long; they are coagulated by heat at 51—53° without change of form, but their double refraction and solubility in water is lost. They contain C, 53·1; H, 7·1; N, 15·9; S, 1·9; O, 22, and ash, 0·22 per cent. The specific rotation is about $-61°$.

August Gürber adds a note that, among other animals, the blood-serum of the rabbit was the only one that yielded crystals. Crystals are best obtained from horse's serum, in which the amount of globulin is small. W. D. H.

Organic Chemistry.

Preparation of Tetramethylethylene. By IVAN KONDAKOFF (*J. pr. Chem.*, 1896, [2], **54**, 429—432).—Of the three methods for the preparation of tetramethylethylene, that of Baeyer and Thiele from pinacone is, in the author's opinion, the most convenient. The yield in this reaction is 25 per cent. less than the theory, the loss being mainly due to the formation of dihexylene and the acetate of dimethylisopropylcarbinol, the latter compound being produced by the action of the zinc bromide on the tetramethylethylene formed. J. F. T.

Action of Alcohols on Tetrachlorethylethylic Ether. By A. PERGAMI (*Gazzetta*, 1896, **26**, ii, 466—477).—Tetrachlorethylethylic ether, $CCl_3\cdot CHCl\cdot OEt$, prepared by Paternò's method (Abstr., 1873, 158) boils at 189·9° (corr.) under 756·9 mm. pressure. On heating it in a closed tube with primary isobutylic alcohol for 3 hours at 200—210°, and distilling the product in a current of steam, *ethylisobutyltrichloracetal*, $CCl_3\cdot CH(O\cdot CH_2\cdot CHMe_2)\cdot OEt$ is obtained; this is a colourless, limpid oil of characteristic ethereal odour, is very soluble in all ordinary solvents, but insoluble in alkalis, boils at 229·31° under 752·72 mm. pressure, has a sp. gr. = 1·186 at 22°, and the normal molecular weight in freezing acetic acid.

Anhydrous chloral readily combines with primary isobutylic alcohol with development of heat, giving a liquid *chloral isobutylate* boiling at about 130°, which, when treated first with phosphorus pentachloride, and then with water, is converted into *tetrachlorethylic isobutylic ether*, $CCl_3\cdot CHCl\cdot O\cdot CH_2\cdot CHMe_2$; it is a limpid oil of camphor-like odour, boils at 215·16° under 761·89 mm., has a sp. gr. of 1·332 at 0° and 1·324 at 27°, and the normal molecular weight in freezing acetic acid. When heated with primary isobutylic alcohol at 200—210° in a closed tube, it yields *di-isobutyltrichloracetal*,

$$CCl_3\cdot CH(O\cdot CH_2\cdot CHMe_2)_2,$$

which resembles its lower homologue in cryoscopic behaviour, boils at 241·75° under 759·57 mm. pressure, and has a sp. gr. of 1·139 at 0°, and 1·133 at 26°.

The tetrachlorether reacts less readily with secondary alcohols, and a poor yield of product is obtained, owing to the occurrence of secondary reactions. On heating secondary isobutylic alcohol with tetrachlorether at 160° for 3—4 hours, a small proportion of a *trichloracetal* of the constitution $CCl_3\cdot CH(O\cdot CHMeEt)\cdot OEt$ is obtained; it boils at 208—215°. If similarly treated, isopropylic alcohol yields a *trichloracetal* of the constitution $CCl_3\cdot CH(O\cdot CHMe_2)\cdot OEt$, which boils at 198—204°. The diethylic ether of glycerol, when heated with tetrachlorether, gave a small quantity of a *substance* boiling at 269—271°, which, however, could not be purified.

Tertiary alcohols do not react with tetrachlorether; on heating trimethylcarbinol with tetrachlorether at 140—150°, the latter decomposes, yielding Paternò's trichloracetal (*loc. cit.*) and chloral alcoholate.
W. J. P.

Action of Potassium Permanganate on the Polyhydric Alcohols and their Derivatives. By LÉON PERDRIX (*Compt. rend.*, 1896, **123**, 945—948).—The author has studied, quantitatively, the action of acidified potassium permanganate solution on the polyhydric alcohols at the boiling temperature. The four following equations are given for (1) glycol, (2) glycerol, (3) erythritol, and (4) mannitol.

(1) $C_2H_6O_2 + 4O = CO_2 + CH_2O_2 + 2H_2O$.
(2) $C_3H_8O_3 + 5O = CO_2 + 2CH_2O_2 + 2H_2O$.
(3) $C_4H_{10}O_4 + 6O = CO_2 + 3CH_2O_2 + 2H_2O$.
(4) $C_6H_{14}O_6 + 8O = CO_2 + 5CH_2O_2 + 2H_2O$.

For each addition, therefore, of the group CH·OH one more oxygen atom is required, and one more molecule of formic acid is produced. The amounts of oxygen required for the oxidation of certain atomic groups under the experimental conditions adopted are presented by the following equations.

(*a*) $CH{\cdot}OH + O = CH_2O_2$. (*b*) $CH_2{\cdot}OH + 2O = 0{\cdot}5CO_2 + 0{\cdot}5CH_2O_2 + H_2O$.
(*c*) $COOH + 0{\cdot}5O = CO_2 + 0{\cdot}5H_2O$. (*d*) $COH + 1{\cdot}5O = CO_2 + 0{\cdot}5H_2O$.
(*e*) $CO + O = CO_2$. (*f*) $CH_2 + 2O = CH_2O_2$.

Knowing the constitution of any given substance, the exact equation representing its oxidation can be constructed by reference to the above numbers, and will be found to agree with the results of experiment; dextrose is a case instanced in the paper. The monhydric alcohols are, however, exceptions to this rule. A. C. C.

The Two Optically Isomeric Methylmannosides. By EMIL FISCHER and LEO BEENSCH (*Ber.*, 1897, **29**, 2927—2931).—Methylmannoside can be formed from mannose by treating it with a strong methyl alcoholic solution of hydrogen chloride. It is, however, more conveniently prepared by means of a modified form of the glucoside synthesis, using an extremely dilute solution of hydrogen chloride in methylic alcohol.

Methyl-d-mannoside, prepared in this way from *d*-mannose, is anhydrous whether crystallised from water or from alcohol. It melts at 190—191° (193—194° corr.) without change, and is soluble in water to the extent of 30·7 parts in 100 at 15°; it has a sp. gr. = 1·473 at 7°/4°, and a rotation $[\alpha]_D^{20^\circ} = +79{\cdot}2^\circ$. The compound shows no tendency towards dimorphism, remaining unchanged after heating for 5 hours at 100°.

Methyl-l-mannoside, prepared from pure *l*-mannose by the same method, has identically the same melting point and crystalline form. Its rotation, $[\alpha]_D^{20^\circ} = -79{\cdot}4^\circ$.

Racemic methylmannoside possesses the property, which has been previously noticed in the case of sodium ammonium racemate, of crystallising unchanged from its aqueous solutions at higher temperatures, whilst at temperatures below 8° its two optically active components crystallise separately. On allowing the mannoside to crystallise at a temperature of about 15°, quadratic leaflets are obtained quite different in form from the optically active compounds; these melt at 165—166° (166·5—167·5° corr.). The sp. gr. determined in benzene = 1·443 at 7°/4°, and it is optically inactive in aqueous solution.

Below 8°, the *d*- and *l*-compounds crystallise separately, and can be separated mechanically. J. F. T.

Allotropy of Sucrose. By FERDINAND G. WIECHMANN (*J. Physical Chem.*, 1896, 1, 69—74).—Solid sugar is known to exist in two allotropic modifications, the crystalline and the amorphous. The amorphous variety is obtained by slowly melting the pure crystalline sugar, carrying the temperature to about 160°, and then allowing the melt to cool. Although this substance can be kept unchanged for some time, its condition seems an unstable one, and the tendency exists to return sooner or later to the crystalline form. To study this transformation more closely, the author prepared specimens of pure amorphous sugar, and of amorphous sugar containing traces of calcium oxide, sodium carbonate, or sodium hydrogen carbonate. These specimens were kept under observation for two months and a half. It was found that, in all the specimens of the pure sugar, no transformation into the crystalline form had occurred, but in all cases in which impurities had been added, a complete change into the crystalline modification had taken place. This was true of specimens which had been kept in the dark, as well as of those which had been exposed to daylight. Wherever crystallisation occurred, it was observed to start from one or more points, and to radiate from these points as centres, giving rise to perfectly circular forms. It seems that the minute amounts of foreign substance had, by their presence, imparted sufficient impulse to the sugar molecules to cause these to assume a more stable state of equilibrium in the crystalline modification. H. C.

Chemical Syntheses by Aid of the Dark Electric Discharge. By SIMA M. LOSANITSCH and MILORAD Z. JOVITSCHITSCH (*Ber.*, 1897, 30, 135—139).—The experiments were carried out in a Berthelot ozoniser, which the authors propose to term an *electriser*. The apparatus was attached to a manometer containing water or mercury, by means of which any contraction could be observed. A current of 3—5 ampères and 70 volts was employed. Under these circumstances, carbonic oxide and water yield formic acid, whilst carbonic anhydride and water yield formic acid and oxygen, the latter then converting a part of the water into hydrogen peroxide. Carbonic oxide and hydrogen yield formaldehyde, which polymerises. Carbonic anhydride and hydrogen yield formic acid. Carbonic oxide and methane react in equal volumes to form acetaldehyde, which, however, polymerises. Carbonic oxide and sulphuretted hydrogen yield sulphur and a reducing substance which is probably thioformaldehyde. Contraction takes place in the reaction between carbonic oxide and hydrogen chloride, probably with formation of formic chloride. Carbonic oxide and ammonia rapidly combine to form formamide, a small amount of hydrogen cyanide being produced at the same time. Carbon bisulphide and hydrogen form hydrogen sulphide and a dark-coloured solid substance, which the authors state to be carbon monosulphide; this substance, together with carbon oxysulphide, is also formed by the action of carbonic oxide on carbon bisulphide. Nitrogen and water form ammonium nitrite, as had previously been found by Berthelot. Unsaturated hydrocarbons are converted into polymeric substances. Thus ethylene yields a thick, yellow liquid which boils above 200°. Benzene gives a thick, sticky, strongly-smelling mass. A. H

New Method of preparing Anhydrides. By GIUSEPPE ODDO and C. MANUELLI. (*Gazzetta*, 1896, **26**, ii, 477—484).—Many dibasic acids, in neutral or feebly alkaline aqueous solution, are converted into their anhydrides by acetic anhydride under certain conditions, the principal of which concern the distance between two carboxyl groups or between a carboxyl group and a carbon atom attached to another radicle such as hydroxyl, amidogen, or nitrilic nitrogen. 1 : 4-Dibasic acids are immediately precipitated from solutions of their barium salts as anhydrides on adding the theoretical quantity of acetic anhydride; phthalic and succinic acids are thus converted, but not isophthalic or terephthalic, oxalic or malonic acids. Salts of 1 : 4-dicarboxylic acids, such as methylsuccinic acid, which contain alkylic groups, are similarly converted into anhydrides, but if, like hydroxy-, dihydroxy-, or amidosuccinic acid or 3-nitrophthalic acid, they contain negative radicles, the anhydride is not formed. An exception is found in the case of naphthalene-1 : 1′-dicarboxylic acid, which readily yields the anhydride; it is of interest to note that camphoric acid is readily converted into its anhydride by the method now described.

Propionic, palmitic, benzoic, cinnamic, and the three nitrobenzoic acids are not thus converted into anhydrides; ortho- and para-amidobenzoic acids are converted into their acetates, whilst the meta-isomeride yields the acetyl derivative. Orthocyanobenzoic acid yields phthalimide, but its meta-isomeride remains unaffected; camphoric mononitrile gives its anhydride.

The explanation of the reaction is evidently that acetic anhydride acts on the salt, forming an unstable mixed anhydride, which then decomposes into the two simple anhydrides. W. J. P.

Composition of Wool-fat. By L. DARMSTAEDTER and ISAAC LIFSCHÜTZ (*Ber.*, 1896, **29**, 2890—2900. Compare Abstr., 1896, i, 522.) —When the soap produced by the hydrolysis of wool-fat is treated with cold alcohol, it yields a solution containing myristic and carnaubic acids, together with three new acids, only one of which has as yet been carefully examined. This acid, to which the authors give the name of *lanopalmic acid*, has the formula $C_{16}H_{32}O_3$, melts at 87—88°, and solidifies in radiating crystals. The melted acid very readily emulsifies with water; it is insoluble in aqueous alkalis, but dissolves in the presence of a little alcohol. The potassium salt appears to be stable in the presence of water, only when the solution is hot, decomposing, as the liquid cools, into an insoluble acid salt and free alkali.

The neutral alcohols from wool-fat have also been further examined, and the presence of unaltered fat, cholesterol and a number of new alcohols has been recognised.

Cerylic alcohol, $C_{27}H_{56}O$, crystallises with $6H_2O$, melts at 77—78°, and loses its water of crystallisation at a slightly higher temperature. It appears to contain a small quantity of a second alcohol, which melts at 69—70°, and is left behind when the mixture is oxidised with chromic acid. The cerylic alcohol is converted by oxidation into cerotic acid.

Carnaubylic alcohol, $C_{24}H_{50}O$, is more readily soluble in alcohol than the foregoing compound; it melts at 68—69°, and is converted by oxidation into carnaubic acid. When this alcohol is crystallised from aqueous alcohol, it dries to a white, transparent mass, which contains 73·3 per cent. of water. A. H.

Compounds of Alloxan and Dimethylalloxan with Semicarbazide. By OTTO BROMBERG (*Ber.*, 1897, **30**, 131—134).—*Alloxansemicarbazide*, $C_5H_9N_5O_6$, is formed by direct union when aqueous solutions of alloxan and semicarbazide hydrochloride are mixed; it crystallises in broad, colourless needles, which gradually decompose when heated. It dissolves in dilute alkalis, but is gradually decomposed by them; when heated with dilute acids, it is converted, with loss of the elements of water, into *anhydroalloxansemicarbazide*, $C_5H_7N_5O_5$, which crystallises in slender, colourless needles; it is also gradually decomposed when heated alone. It dissolves in alkalis, reduces Fehling's solution, and when treated with hydrochloric acid and potassium chlorate, gives a solution which yields the murexide reaction, so that it is probably a derivative of alloxan, and not of alloxanic acid. Dimethylalloxan reacts with semicarbazide hydrochloride, with elimination of the elements of water, forming *dimethylalloxansemicarbazide*, $C_7H_{11}N_5O_5$; this crystallises in oblique, pointed tablets, and gradually decomposes when heated. Dilute acids convert it, with loss of a second molecule of water, into *anhydrodimethylalloxansemicarbazide*, $C_7H_9N_5O_4$; this is also formed when dimethylalloxan and semicarbazide hydrochloride are boiled together in aqueous solution. It crystallises in slender, six-sided plates, and, like the other compounds, decomposes gradually when heated. Aqueous alkalis convert it into a *substance*, $C_6H_{11}N_5O_3$, which crystallises in slender, colourless needles, decomposes at about 270°, and yields a crystalline sodium salt. The constitution of these compounds has not yet been ascertained. A. H.

Mesitylene from Acetone. By AD. LUCAS (*Ber.*, 1896, **29**, 2884—2887).—The conclusion of V. Meyer and Molz (this vol., i, 142) is confirmed, that mesitylene, formed by condensation from acetone, contains no isomeric trimethylbenzene. The action of sulphuric acid brings about no molecular transformation. as it is found that, when pure mesitylene is sulphonated and then regenerated from the sulphonic acid, it boils at exactly the same temperature as before. It is known, however, that some 1 : 2 : 3 : 4-trimethylbenzoic acid is formed when mesitylene is caused to condense with acetic chloride in the presence of aluminium chloride, and the product is oxidised. A partial molecular transformation must, therefore, have resulted from the action of the acetic chloride.

Commercial mesitylene contains very little impurity, although when distilled it passes over within a fairly wide interval of temperature. Such impurity as it does contain is of the nature of an olefine, for it unites directly with bromine in the cold. C. F. B.

Technical Uses of Ortho- and Para-nitrophenol. By LUDWIG PAUL (*Zeit. angw. Chem.*, 1896, 587—595).—The author finds that the preparation of orthonitrophenol from the corresponding sulphonic acid, by means of superheated steam, is not to be recommended for use on a commercial scale, on account of the poor yield (some 25 per cent.). The conversion of orthonitrophenol into orthonitranisoil, by heating it with methylic chloride under pressure, is described, and also the conversion of the nitranisoil into dianisidine.

The author has also attempted to prepare diphenetidine and dianisidine from paraphenolsulphonic acid. This was first nitrated, and the orthonitrophenolparasulphonic acid thus obtained was converted into its methylic ether, the sodium salt of which is readily soluble in 80 per cent. alcohol. The corresponding ethylic ether, when distilled with superheated steam, gave orthonitrophenol, and not orthonitranisoil. When reduced with stannous chloride in acid solution, the ethylic ether was converted into phenetidinesulphonic acid, but on reduction with zinc dust in alkaline or acid solution, ethoxyazobenzenedisulphonic acid,

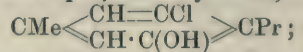
$$N_2[C_6H_3(OEt)\cdot SO_3H]_2,$$

was formed. The latter, on further reduction with stannous chloride and hydrochloric acid, yielded phenetidinemetadisulphonic acid, and this, when heated with water under pressure at 170° gave the corresponding monosulphonic acid. Directions are also given for the reduction of orthonitrophenol to the corresponding amidophenol on the large scale, by means of hydrogen sulphide, or on the small scale by means of stannous chloride; also of paranitrophenol to paramidophenol, by means of sodium sulphide and hydrogen chloride in the presence of tin. The preparation of paranitrophenetoil, of paramidophenetoil, and of phenacetin, are also described. J. J. S.

Mono- and Di-chloroparacresols. By GIROLAMO MAZZARA and MANFREDO LAMBERTI-ZANARDI (*Gazzetta*, 1896, **26**, ii, 399—403).—Paracresol is readily acted on by sulphuryl chloride, either alone or in chloroform solution, and after warming and adding sodium carbonate, the product yields 3-chloro-1 : 4-cresol [Me = 1], on distillation in a current of steam (Schall and Dralle, Abstr., 1885, 145). With two molecular proportions of sulphuryl chloride, Claus and Riemann's 2 : 5-dichloro-1 : 4-cresol is obtained (Abstr., 1883, 1111).

The authors consider that these facts show that the conclusions of Peratoner and Finocchiaro (Abstr., 1894, i, 368), and of Peratoner and Genco (Abstr., 1895, i, 342), are unwarranted. The phenols do not react with sulphuryl chloride in the ketonic form, and sulphuryl chloride cannot be applied to the diagnosis of phenolic hydroxyl. W. J. P.

Monochlorothymol and Dichlorocymene. By O. BOCCHI (*Gazzetta*, 1896, **26**, ii, 403—406).—Thymol and sulphuryl chloride react readily in molecular proportion, yielding *monochlorothymol*,



$$\mathrm{CMe}\left<\begin{matrix}\mathrm{CH{=}CCl}\\ \mathrm{CH\cdot C(OH)}\end{matrix}\right>\mathrm{CPr};$$

on treating the product with warm, dilute potash, separating the clear liquid, and treating with dilute sulphuric acid, solid chlorothymol is obtained; it crystallises from light petroleum in transparent, rhombic plates, melting at 58—60°. The *acetyl* derivative, $C_{14}H_{12}ClO_2$, obtained by the action of acetic anhydride on the chlorothymol, is a colourless liquid, whilst the *benzoyl* derivative, $C_{17}H_{17}ClO_2$, prepared by heating a potash solution of chlorothymol with benzoic chloride on the water bath, forms tetragonal crystals melting at 71—73°.

On gradually heating a mixture of chlorothymol with phosphorus pentachloride to 230°, reaction occurs, and on treating the product with sodium carbonate, and distilling in a current of steam, the dichlorocymene, $CMe<\genfrac{}{}{0pt}{}{CCl:CH}{CH\cdot CCl}>CPr$, prepared by von Gerichten (Abstr., 1878, 570), is obtained; it boils at 240—243° (corr.), and its constitution is established by the fact that it yields paradichloroterephthalic acid when heated with dilute nitric acid at 180—200° in a closed tube.

W. J. P.

Blue Dye from Quinone. By JAMES LEICESTER (*Chem. News*, 1896, **74**, 236).—*Dinitrodianilidoquinone*, $C_{18}H_{12}N_4O_6$, probably

$$C_6H_2O_2(NH\cdot C_6H_4\cdot NO_2)_2,$$

obtained by heating benzoquinone in glacial acetic acid solution with orthnitraniline; it melts at 305°. When reduced by means of alcoholic ammonium sulphide, it yields a dark green powder, $C_{18}H_{10}N_4O_2$, called *istarine* which dissolves in acetic acid with an intense blue colour, red by reflected light, and dyes silk and wool a fast blue. Dilute sulphuric acid produces a strong fluorescence in the acetic acid solution.

D. A. L.

Fate of Cholesterol in the Animal Organism. By STANISLAS BONDZYŃSKI and V. HUMNICKI (*Zeit. physiol. Chem.*, 1896, **22**, 396—416). (For the physiological part of this paper, see this vol., ii, 153).—*Coprosterol*, $C_{27}H_{48}O$, is formed by the passage of cholesterol through the body; it crystallises in long, slender needles, melts at 95—96° and has $[\alpha]_D = +24°$. It gives reactions similar to those of cholesterol, of which it seems to be the dihydro-derivative. The *acetyl* derivative forms needles, and melts at 85°; the *bromacetyl* derivative is crystalline, and melts at 118°; the *propionyl* derivative crystallises in needles melting at 92°; the *benzoyl* derivative forms rectangular plates, melting at 114—115°. The *cinnamoyl* derivative crystallises in rectangular prisms, melts at 169°, and yields a crystalline *dibromide* melting at 165—166°. *Cinnamoylcholesterol*, prepared for purposes of comparison, crystallises in characteristic tablets, melts at 149°, and yields a *tetrabromide* melting at 139°.

Hippocoprosterol, $C_{27}H_{54}O$ or $C_{27}H_{56}O$, is obtained from the faeces of the horse; it forms microscopic needles, and melts at 74—75°.

W. D. H.

Hæmosterol, a New Constituent of Blood. By KARL HÜRTHLE (*Chem. Centr.*, 1896, i, 562; from *Schles. Ges. f. vaterländ. Kult. Med. Sekt.*, 1895).—The author has isolated a new compound, *hæmosterol*, from the fresh blood of various animals, in which it is present to the amount of about 0·1 per cent., and also from blood serum. It crystallises in optically uniaxial needles, which melt at 37—42°, and the molten mass, on cooling, shows a blue fluorescence. It is easily soluble in ether and chloroform and slightly so in hot alcohol. Solutions of the crystals are lævorotatory. To this substance, the author ascribes the formula $C_{20}H_{31}(OH)$, and regards it as allied to cholesterol, the characteristic reactions of which it gives with slight variations. Attempts to obtain benzoyl derivatives were unsuccessful. Three different substances, containing respectively 80, 82, and 84 per cent. of carbon, and melting at 37—46°, were obtained from the blood serum of horses.

E. W. W.

Paranitrobenzyl Bases. By CARL PAAL & HERMANN SPRENGER (*Ber.*, 1897, **30**, 61—70).—These were prepared, in the case of the methyl-, ethyl-, and propyl-amine derivatives, by heating paranitrobenzylic chloride with a 33 per cent. aqueous solution of the amine for 2 hours in a sealed tube at 110—120°; in the case of the *i*-amylamine, allylamine, and aniline derivatives, by boiling a concentrated alcoholic solution of the chloride and the amine in a reflux apparatus. In the first cases, a tertiary base is the chief product, the secondary base being formed in smaller quantity, even when a large excess of the amine is used; in the other cases, the secondary base is formed in larger quantity. The two products are easily separated, as the tertiary amine has but very feebly basic properties, whereas the secondary amine forms stable salts.

Paranitrobenzylmethylamine, $NO_2 \cdot C_6H_4 \cdot CH_2 \cdot NHMe$, is a yellow syrup; the *hydrochloride* melts at 219°, the yellowish-red *platinochloride* at 220°, and the oxalate at 188°. *Bis-paranitrobenzylmethylamine*, $(NO_2 \cdot C_6H_4 \cdot CH_2)_2NMe$, forms yellow needles melting at 104°.

Paranitrobenzylethylamine, $NO_2 \cdot C_6H_4 \cdot CH_2 \cdot NHEt$, is a yellow, syrupy oil; the *hydrochloride* and *oxalate* melt at 226° and 207° respectively. The reddish-yellow *platinochloride* was also prepared. *Bis-paranitrobenzylethylamine*, $(NO_2 \cdot C_6H_4 \cdot CH_2)_2NEt$, crystallises from ether in orange-red crystals resembling rhombohedra; from alcohol, in yellow plates that melt at 68°.

Paranitrobenzylpropylamine, $NO_2 \cdot C_6H_4 \cdot CH_2 \cdot NHPr$, is a yellow syrup; the *hydrochloride* melts at 225°, the yellow *platinochloride* at 177°, and the *oxalate* at 228°. *Bis-paranitrobenzylpropylamine*,

$$(NO_2 \cdot C_6H_4 \cdot CH_2)_2NPr,$$

is yellow, and melts at 77°.

Paranitrobenzylisoamylamine, $NO_2 \cdot C_6H_4 \cdot CH_2 \cdot NH \cdot C_5H_{11}$, forms a yellow syrup; the *hydrochloride* melts at 204°, the orange *platinochloride* at 206°, the *oxalate* at 223°, and the yellow *picrate* at 144°. The base itself is reduced by zinc dust and acetic acid, at a temperature not exceeding 30°, to *paramidobenzylisoamylamine*,

$$NH_2 \cdot C_6H_4 \cdot CH_2 \cdot NH \cdot C_5H_{11},$$

an unstable oil. *Bis-paranitrobenzylisoamylamine*,

$$(NO_2 \cdot C_6H_4 \cdot CH_2)_2N \cdot C_5H_{11},$$

is yellow, and melts at 57°.

Paranitrobenzylallylamine, $NO_2 \cdot C_6H_4 \cdot CH_2 \cdot NH \cdot C_3H_5$, is a yellow oil; the *hydrochloride* melts at 226°, the reddish-yellow *platinochloride* at 174°, the *oxalate* at 224°, and the yellow *picrate* at 146°. *Bis-paranitrobenzylallylamine*, $(NO_2 \cdot C_6H_4 \cdot CH_2)_2N \cdot C_3H_5$, is yellowish, and melts at 46°.

Paranitrobenzylaniline, $NO_2 \cdot C_6H_4 \cdot CH_2 \cdot NHPh$, is orange-coloured, and melts at 72°; it is reduced by iron filings and acetic acid to *paramidobenzylaniline*, $NH_2 \cdot C_6H_4 \cdot CH_2 \cdot NHPh$, a yellow oil which deposited a few crystals melting at 49—50°, and yields a yellow, granular, amorphous *hydrochloride* (with 2HCl). *Bis-paranitrobenzylaniline*, $(NO_2 \cdot C_6H_4 \cdot CH_2)_2NPh$, is greenish-yellow, and melts at 169°.

C. F. B.

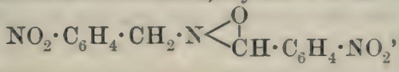
Action of Orthonitrobenzylic Chloride on Hydroxylamine. By CARL PAAL and H. POLLER (*Ber.*, 1897, **30**, 58—60).—When orthonitrobenzylic chloride is heated with hydroxylamine in alcoholic solution, yellow crystals of *bis-orthonitrobenzylhydroxylamine*,

$$(NO_2\cdot C_6H_4\cdot CH_2)_2N\cdot OH,$$

are obtained, in addition to an oil which is possibly the mono-derivative. The crystals melt at 124° ; the *hydrochloride* is decomposed by water ; the *acetyl* derivative melts at 134° ; reduction with zinc dust and alcoholic hydrochloric acid at a temperature not exceeding 40°, leads to the formation of *bis-orthamidobenzylhydroxylamine*,

$$(NH_2\cdot C_6H_4\cdot CH_2)_2N\cdot OH,$$

melting at 142°, and treatment with hydrochloric acid and sodium nitrite, in alcoholic solution, to yellow *orthonitrobenzylorthonitroisobenzaldoxime*,



$$NO_2\cdot C_6H_4\cdot CH_2\cdot N\lt\begin{matrix}O\\|\\CH\cdot C_6H_4\cdot NO_2\end{matrix},$$

melting at 150°.

C. F. B.

The "Diazo" Controversy. By CHRISTIAN W. BLOMSTRAND (*J. pr. Chem.*, 1896, [2], **54**, 305—339).—An historical and critical account of the recent work of Hantzsch and of Bamberger on the constitution of the diazo-compounds.

J. F. T.

Diazosulphonates and Free Diazosulphonic Acids. By ARTHUR R. HANTZSCH and M. SCHMIEDEL (*Ber.*, 1897, **30**, 71—88. Compare Abstr., 1895, i, 180).—Potassium *syn*-diazosulphonates are obtained by dissolving or suspending the amine in water and hydrochloric (or occasionally sulphuric) acid, diazotising the well-cooled solution with sodium nitrite, and pouring the mixture into a well-cooled solution of potassium sulphite. They vary in colour from light to dark orange ; some can be dried on a porous plate over phosphoric anhydride in the dark ; others at once undergo a molecular transformation under these circumstances, and even explode spontaneously ; the darker-coloured salts seem to be less stable than the lighter ones. In aqueous solution, even at 0°, they are all transformed into the stereoisomeric *anti*-diazosulphonates, but with very varying rapidity. The *syn*-diazosulphonate of orthochlorobenzene is comparatively stable, as is also that of 2 : 4-di-iodobenzene ; those of parachloro-, parabromo-, and 2 : 4-dibromo-benzene are less stable ; whilst those containing an alkyl group, such as the salts of para- and meta-toluene, of xylene, pseudocumene, mesitylene, and orthanisidine, are so unstable that it is impossible to isolate a pure *syn*-salt, and the same is true even of dibromoparatoluene and dibromorthotoluene, which also contain halogen atoms. The *syn*-diazosulphonate of sulphanilic acid was only obtained in solution. Lastly, the *syn*-diazosulphonates of tribromobenzene and naphthalene (α and β) cannot be made to yield *anti*-salts ; in the last two cases, $\alpha\alpha$- or $\beta\beta$-azonaphthalene is respectively formed. To prepare an *anti*-salt, the *syn*-salt is suspended in about 30 times its weight of water, and the solution allowed to remain at the ordinary temperature for an hour, during which time it is frequently shaken ; it is then boiled, and more water added, if necessary, to dissolve the salt ; the *anti*-salt crystallises out as the solution cools. These *anti*-salts are yellow or reddish-yellow in colour ; with barium chloride and silver nitrate, they yield respectively barium and silver salts that are sparingly soluble in water. The potassium *syn*-diazosulphonates do not yield precipitates of such salts; on the other hand, unlike the *anti*-salts, they condense with β-naphthol and similar substances, forming azo-dyes.

Since the potassium *syn*-diazosulphonates can be titrated with iodine just as if they were sulphites, whilst the *anti*-salts do not act on iodine, the rate of transformation of *syn*- into *anti*-salt in an aqueous solution can be measured (usually at 0°) by titrating, from time to time, an aliquot portion of the solution with iodine. In the case of *syn*-diazobenzenesulphonate, about 10 per cent. is converted in the first minute; in the case of the orthochloro- or 2 : 4-di-iodo-benzene salts, only about 80 per cent. was converted at the end of a quarter of an hour. The reaction is not so simple as it seems, for the amounts transformed do not agree with those calculated on the assumption that the amount transformed at any time is proportional to the concentration of the unchanged substance at that time; the rate of transformation diminishes as the transformation proceeds.

The free *antidiazosulphonic acids* of *parabromobenzene*, 2:4-*dibromobenzene*, and *paratoluene* were obtained by suspending the silver anti-salts in water, decomposing them with the calculated quantity of hydrochloric acid, filtering, and allowing the filtrate to evaporate over sulphuric acid at a low temperature. They form yellow, deliquescent needles, and are all unstable; the last melts at 112—114°. C. F. B.

Action of Potassium Sulphite on Nitrodiazonium Salts. By Arthur R. Hantzsch and H. Borghaus (*Ber.*, 1897, **30**, 89—92. Compare Bamberger and Kraus, Abstr., 1896, i, 610).—The isomeric nitrobenzenediazonium salts, chlorides as well as nitrates, are extremely unstable. With potassium sulphite, they yield yellow *syn*-diazosulphonates; these explode, even when moist; when allowed to remain in contact with aqueous potassium carbonate, they are transformed into the *anti*-salts; and when treated with an excess of potassium sulphite, they yield hydrazinedisulphonates, $NO_2\cdot C_6H_4\cdot N(SO_3K)\cdot NH\cdot SO_3K$, from which boiling with dilute hydrochloric acid sets free the hydrazines.

Paranitrobenzenediazosulphonic acid can be obtained in red, efflorescent, unstable crystals by treating the yellow anti-silver salt (which explodes at 140—141°) with the calculated amount of hydrochloric acid, and evaporating the filtrate at 0° under diminished pressure.

Potassium metanitrobenzenesyndiazosulphonate is extremely unstable, exploding even when moist and at 0°; the *anti*-salt is yellow. *Potassium metanitrophenylhydrazinedisulphonate* crystallises with $2H_2O$, and is red; recrystallisation from water converts it gradually into a yellow salt, apparently $NO_2\cdot C_6H_4\cdot NH\cdot NH\cdot SO_3K + H_2O$.

The *orthonitrobenzene* derivatives resemble the above in properties.

Diazosulphonates of dinitrophenol and of two nitrotoluenes were also prepared; the first crystallises in yellow plates or red needles, apparently with $2H_2O$ in both cases; the last two call for no particular remark. C. F. B.

Bis-Diazonium Salts. By Arthur R. Hantzsch and H. Borghaus (*Ber.*, 1897, **30**, 92—93).—Paraphenylenediamine yields the yellowish, very explosive *bisdiazonium chloride*, $C_6H_4(N_2Cl)_2$, when treated with nitrogen trioxide in hydrochloric acid solution at 0°; the *sulphate* is more stable. Metaphenylenediamine also yields similar derivatives; orthophenylenediamine does not. Attempts to convert these salts into cyanides or sulphonates were unsuccessful, they are completely decomposed. C. F. B.

Oximes of the Fatty Aromatic Ketones containing the higher Alkyls. The Stereochemistry of Nitrogen. By ADOLPH CLAUS and HERMANN HÄFELIN (*J. pr. Chem.*, 1896, [2], **54**, 391—405).—Further instances are brought forward tending to show that, contrary to van't Hoff's law, oximes containing a fatty and an aromatic group on the carbon atom of the oxime residue do not exist in two forms.

Metaxylyl heptadecyl ketone, (4-*stearometaxylone*),

$$C_6H_3Me_2\cdot CO\cdot C_{17}H_{35}\ [Me_2 : CO = 1 : 3 : 4],$$

is prepared from metaxylene and stearic chloride in the presence of aluminium chloride; when recrystallised from alcohol, it forms white, vitreous plates melting at 39°, distils at 260—280° under 15 mm. pressure, and yields 2 : 4-dimethylbenzoic acid (m. p. 126°) on oxidation with dilute nitric acid. This compound, like all ketones of this class, expands on solidifying.

Metaxylyl heptadecyl ketoxime, prepared in the usual way, separates from solvents as an oil which solidifies on standing; it melts at 45°, and is quantitatively hydrolysed when heated with hydrochloric acid at 125—130°.

On treatment with phosphorus pentachloride or sulphuric acid, the oxime undergoes the Beckmann rearrangement, being converted into *stearylmetaxylidide*, $C_6H_3Me_2\cdot NH\cdot CO\cdot C_{17}H_{35}$, which can also be prepared from stearic chloride and metaxylidine. It melts at 95° after recrystallisation from alcohol, and as on hydrolysis it yields only stearic acid and metaxylidine, it must be homogeneous. If the theoretical stereochemical form really existed, it should give, on rearrangement and hydrolysis, xylenecarboxylic acid and heptadecylamine; no trace of these, however, could be found.

Phenyl heptadecyl ketone (*stearophenone*), $C_6H_5\cdot CO\cdot C_{17}H_{35}$, prepared in the same way, crystallises from alcohol in snow-white leaflets, melts at 59°, and distils at 250—270° under 18 mm. pressure. The *oxime* crystallises from the same solvent in small leaves melting at 53°, and on rearrangement yields the anilide of stearic acid, melting at 93°.

Paraxylyl heptadecyl ketone, (2-*stearoparaxylone*),

$$C_6H_3Me_2\cdot CO\cdot C_{17}H_{35}\ [Me_2 : CO = 1 : 4 : 2],$$

from paraxylene and stearic chloride, crystallises from alcohol in colourless leaflets melting at 57°. The *oxime*, like the meta-compound separates from solvents as an oil, which solidifies after a time; it melts at 50°. No trace of paraxylenecarboxylic acid could be obtained on rearrangement and hydrolysis.

Similarly, *paratolyl heptadecyl ketoxime*, which crystallises from alcohol in glistening needles, melting at 64°, and *paratolylpentadecyl ketoxime* gave only stearylparatoluide and palmitylparatoluide respectively on rearrangement and hydrolysis.

Mesityl pentadecyl ketone, (*palmitomesitone*), $C_6H_2Me_3\cdot CO\cdot C_{15}H_{31}$ $[Me_3 : CO = 1 : 3 : 5 : 2]$, formed from mesitylene and palmitic chloride in the presence of aluminium chloride, crystallises from alcohol in white leaflets, melts at 35°, and distils at about 280° under 15 mm. pressure. Like all known ketones containing a mesityl residue, it does not yield an oxime with hydroxylamine. J. F. T.

A Curious Instance of Molecular Rearrangement. By LUDWIG CLAISEN (*Ber.*, 1897, **29**, 2931—2933).—Like acetone, acetophenone condenses with ethylic orthoformate, with the formation of *acetophenone orthodiethylic ether*, $CMePh(OEt)_2$, a compound which distils unchanged at 107° under a pressure of 17 mm., but when distilled under atmospheric pressure, it loses the elements of a molecule of alcohol, and passes into *iso-acetophenone ethylic ether*, $OEt{\cdot}CPh{:}CH_2$, an oil boiling at 209°. If this be now slightly superheated (that is, boiled for some hours under a pressure of 2 atmospheres), rearrangement ensues with the production of phenyl propyl ketone, $CH_2{:}CPh{\cdot}OEt = COPh{\cdot}CH_2Et$.

In the same way, phenyl ethyl ketone can be prepared from acetophenone orthodimethylic ether, and phenyl butyl ketone from the orthodipropylic ether. Benzophenone also, on treatment with methylic orthoformate, yields *benzophenone orthodimethylic ether*, $CPh_2(OMe)_2$, melting at 107°, and with ethylic orthoformate, *benzophenone orthodiethylic ether*, melting at 52°.

The ketone ortho-ethers yield ketoneanilides when boiled with aniline. The *anilide of acetone*, $CMe_2{:}NPh$, is a liquid boiling at 195°, whilst the *anilide* of *acetophenone*, $CMePh{:}NPh$, is a solid melting at 41°, and boiling without decomposition at 310°.

From pyruvic acid, the following compounds can be obtained on condensation with ethylic orthoformate. *Ethylic α-diethoxypropionate*, $CMe(OEt)_2{\cdot}COOEt$, an oil boiling at 191°, which on treatment with phosphoric anhydride passes into *ethylic α-ethoxyacrylate*,

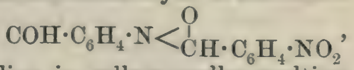
$$CH_2{:}C(OEt){\cdot}COOEt,$$

boiling at 180°, and this on hydrolysis yields *α-ethoxyacrylic acid*, $CH_2{:}C(OEt){\cdot}COOH$, crystallising in glistening needles, and melting at 62°. This acid is quite different from the α-ethoxyacrylic acid, melting at 108°, obtained by Otto from αα-dichloropropionic acid, and by Merz from αα-dibromopropionic acid. The two compounds must necessarily be α-ethoxyacrylic acids, and this is, therefore, an interesting instance of isomerism, which is not capable of explanation according to the existing theories. Ethylic orthoformate combines with all aldehydes, both fatty and aromatic, with the production of compounds of which several are still under investigation. J. F. T.

Electrolytic Reduction of Aromatic Nitro-compounds. By LUDWIG GATTERMANN (*Ber.*, 1896, **29**, 3034—3037. Compare Abstr., 1893, i, 566, and Abstr., 1894, i, 72, 502).—[With A. E. LOCKHART 5 : 2-*Amidohydroxyacetophenone* is obtained by electrolytic reduction of metanitroacetophenone, and crystallises from water in golden-yellow leaflets melting at 110° ; the aqueous solution develops a brownish-red coloration with ferric chloride, and the alkaline solutions are intensely yellow, becoming dark brown on exposure to air.

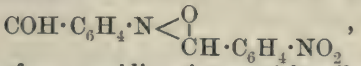
[With C. WEINLIG] 5 : 2-*Amidohydroxybenzophenone* is obtained from metanitrobenzophenone ; it crystallises from water in orange-coloured plates, and melts at 107°.

5:2-*Amidohydroxyphenyl paratolyl ketone*, obtained by reducing metanitrophenyl paratolyl ketone; crystallises from water in golden-yellow needles, and melts at 93°. M. O. F.



Electrolytic Reduction of Aromatic Nitro-compounds. By Ludwig Gattermann [and Alway] (*Ber.*, 1896, **29**, 3037—3040. Compare foregoing abstract).—When paranitrobenzaldehyde is submitted to electrolytic reduction, the *compound* $COH\cdot C_6H_4\cdot N<\begin{matrix}O\\ |\\ CH\cdot C_6H_4\cdot NO_2\end{matrix}$, is produced; it crystallises from pyridine in yellow needles melting at 224°. *Paranitrosobenzaldehyde*, which is obtained on oxidising this substance with ferric chloride, crystallises from glacial acetic acid in yellow needles, and melts to a green liquid at 137—138°.

Metanitrobenzaldehyde also yields, on reduction, a *compound*,



$$COH\cdot C_6H_4\cdot N<\begin{matrix}O\\ |\\ CH\cdot C_6H_4\cdot NO_2\end{matrix},$$

which crystallises from pyridine in greyish-yellow aggregates, and melts at 191°; oxidation with ferric chloride converts it into metanitrosobenzaldehyde (compare Bamberger, Abstr., 1895, i, 217). M. O. F.

Electrolytic Reduction of Aromatic Nitro-compounds. By Ludwig Gattermann [Würst and Bohn] (*Ber.*, 1896, **29**, 3040—3042. Compare foregoing abstracts).—When nitrobenzene is submitted to electrolytic reduction in presence of benzaldehyde, the benzylidene derivative of phenylhydroxylamine (Abstr., 1894, i, 412) is produced. The *benzylidene* derivatives of ortho-, meta-, and para-tolylhydroxylamine melt at 119—120°, 95—96°, and 123—124° respectively; the *benzylidene* derivative of paraxylylhydroxylamine crystallises from petroleum in colourless needles, and melts at 129—130°.

The *benzylidene* derivative of metahydroxylamidobenzoic acid is obtained from metanitrobenzoic acid and benzaldehyde; it melts and decomposes at 200°. M. O. F.

Action of Hydroxylamine on Benzylideneacetophenone. By Adolph Claus (*J. pr. Chem.*, 1896, [2], **54**, 405—414).—The true oxime of benzylideneacetophenone is in no case formed when hydroxylamine acts on the ketone, but at the moment of its formation it either undergoes an intramolecular transposition, or combines again with another molecule of the hydroxylamine. In the first case, the product has the same composition as the true oxime, but none of the reactions characteristic of an oxime; whilst in the second, two products are formed, which, although they behave as oximes, have a different empirical formula from the true oxime.

All three compounds are always obtained when hydroxylamine acts on the ketone; they can be separated in the following way.

I. Water is added to the strongly alkaline mixture until a precipitate is no longer produced; the precipitate, after repeated recrystallisation from alcohol, melts at 73°, and is evidently *αγ-diphenyldihydroisoxazole* since, it is readily converted into αγ-diphenylisoxazole on oxidation with chromic acid in acetic acid solution.

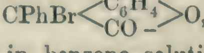
II. On neutralising the alkaline filtrate with hydrochloric acid, a precipitate is produced consisting of two substances, which can be separated by treatment with hot benzene. The insoluble portion separates from alcohol in fine, colourless crystals, melting at 218°, whilst that dissolved by the hot benzene crystallises out on cooling in slender needles, melting at 150°. They both behave similarly, yielding acetyl compounds with acetic anhydride, and isoxazole on oxidation; they are also isomeric. A further description of their properties is reserved.

3 : 5-*Diphenylisoxazole* is obtained as described above. It is a very stable compound crystallising in colourless glistening leaflets melting at 140°. J. F. T.

Calcium Orthoethylbenzoate, and the author's Theory of Water of Crystallisation. By THEODOR SALZER (*Ber.*, 1897, **30**, 103—104).—Calcium orthoethylbenzoate is described by Giebe (this vol., i, 62) as containing $3H_2O$, whereas, according to the author's theory, it should only crystallise with $2H_2O$ (Abstr., 1896, ii, 415). On examination, the salt was found to contain a small amount of some acid of lower molecular weight, and, after five recrystallisations, separated out with only $2H_2O$. A. H.

Preparation of Mandelic Acid. By CARL PAPE (*Chem. Zeit.*, 1896, **20**, 90).—Mandelonitrile is readily obtained by mixing an aqueous solution of the sodium hydrogen sulphite compound of benzaldehyde with a concentrated aqueous solution of potassium cyanide. The nitrile is deposited in a pure form as a yellow oil, and the yield is extremely good. In actual practice, it is not necessary to use sufficient water to dissolve the whole of the sodium hydrogen sulphite compound. The nitrile is easily converted into the acid by treating it with thrice its volume of concentrated hydrochloric acid, much heat being developed by the action. J. J. S.

Condensation of Mandelic Acid with Phenols. II. By AUGUSTIN BISTRZYCKI and J. FLATAU (*Ber.*, 1897, **30**, 124—131. Compare Abstr., 1895, i, 419). When crude orthohydroxydiphenylacetic lactone is washed with sodium carbonate solution and the liquid acidified, *parahydroxydiphenylacetic acid*, $OH\cdot C_6H_4\cdot CHPh\cdot COOH$, is precipitated; when pure, this crystallises in concentric groups of flat needles, melting at 173°, and is a comparatively strong acid. The basic barium salt, $BaC_{14}H_{10}O_3 + 4H_2O$, separates in nodular crystals, which lose $3H_2O$ at 125°.

Orthobenzoxydiphenylacetic acid, $OBz\cdot C_6H_4\cdot CHPh\cdot COOH$, crystallises in groups of tablets, and melts at 152.° *Orthohydroxydiphenylbromacetic lactone*,  $CPhBr<^{C_6H_4}_{CO\,-}>O$, is formed by the action of bromine on the lactone in benzene solution; it crystallises in small tablets, and melts at 70°; when boiled with alcohol, the bromine atom is removed and *ethoxyorthohydroxydiphenylacetic lactone* is formed; this crystallises in small prisms melting at 85—86°. It is sparingly soluble in sodium carbonate, readily in aqueous potash, yielding a solution from which acids precipitate *ethoxyorthohydroxydiphenylacetic acid*,

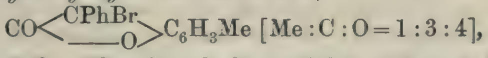
$$OH\cdot C_6H_4\cdot CPh(OEt)\cdot COOH;$$

this crystallises in microscopic needles, and melts and decomposes at 131°.

Mandelic acid does not appear to undergo condensation with nitrophenols or phenolic ethers, but reacts with many of the homologues of phenol.

Basic barium phenylparahydroxytolylacetate, $C_{15}H_{12}O_3Ba + 4H_2O$, resembles the corresponding diphenyl compound.

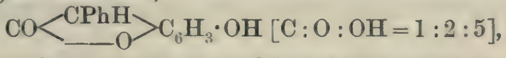
Phenylparahydroxytolylbromacetic lactone,



$$\mathrm{CO}{<}\begin{smallmatrix}\mathrm{CPhBr}\\ \text{———}\mathrm{O}\end{smallmatrix}{>}\mathrm{C_6H_3Me}\ [\mathrm{Me : C : O} = 1 : 3 : 4],$$

melts at 94—96°. *Phenylmetahydroxytolylacetic lactone* [Me : C : O = 1 : 2 : 3 or 1 : 4 : 3] crystallises in needles melting at 122°, and has not hitherto been converted into the corresponding acid.

Phenylquinylacetic lactone,



$$\mathrm{CO}{<}\begin{smallmatrix}\mathrm{CPhH}\\ \text{———}\mathrm{O}\end{smallmatrix}{>}\mathrm{C_6H_3{\cdot}OH}\ [\mathrm{C : O : OH} = 1 : 2 : 5],$$

crystallises in nodular aggregates melting at 153—154°.

Phenyl-β-hydroxynaphthylacetic lactone forms slender prisms, melting at 184°.

A. H.

Elimination of Sulphur from Resorcinoldithiocarboxylic Acid. By Carl Schall (*J. pr. Chem.*, 1896, [2], **54**, 415—421).—Resorcinoldithiocarboxylic acid is entirely freed from sulphur on treatment with alcoholic potash and excess of methylic iodide, although if the latter is not added it remains unchanged. On reduction with sodium amalgam and acidifying, a yellowish-white precipitate is produced, which yields an acetyl compound, evidently *tetracetoxydibenzyl*,

$$C_2H_4[C_6H_3(OAc)_2]_2\ [(OAc)_4 = 2 : 4 : 2' : 4'],$$

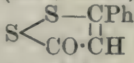
melting at 105—112°; from the filtrate, excess of bromine precipitates a red-brown powder, which on acetylation and recrystallisation from glacial acetic acid melts at 215—220°; it is probably *dibromotetracetoxydibenzyl*, $C_2H_4[C_6H_2Br(OAc)_2]_2$. On reducing it in acid solution (zinc and acetic acid), cresorcinol melting at 100—104° is obtained. It is, therefore, possible by this means to introduce a methyl group into the resorcinol nucleus.

Di-α-hydroxynaphthylthione bisulphide,

$$S_2(CS{\cdot}C_{10}H_6{\cdot}OH)_2\ [OH : CSS : 1 : 2],$$

is obtained by heating α-naphthol with potassium sulphide and carbon bisulphide for 12 hours on the water bath. It is a red powder which on acetylation gives a methylation product soluble in alkalis.

J. F. T.



Action of Sulphur on Unsaturated Organic Compounds. Bisulphide of Thiobenzoylthiacetic Acid. By Eugen Baumann and Emil Fromm (*Ber.*, 1897, **30**, 110—117).—The *bisulphide of thiobenzoylthioacetate* $\mathrm{S}{<}\begin{smallmatrix}\mathrm{S{-}CPh}\\ \mathrm{CO{\cdot}CH}\end{smallmatrix}$, is formed when ethylic cinnamate is heated with sulphur; it crystallises in yellowish, almost odourless tablets, melts at 117°, and when distilled with aqueous potash, it yields acetophenone, a proof that one of the sulphur atoms is united with the carbon atom which is directly combined with the benzene nucleus. Phenylhydrazine converts the bisulphide into bisdiphenylpyrazolone, $C_{30}H_{22}N_4O_2$. The bisulphide is accompanied by small amounts of thioacetophenone, ethylic phenylpropionate and diphenylthiophen. A. H.

Condensation of Ethereal Salts of γ-Disubstituted Itaconic Acids with Aldehydes and Ketones. By HANS STOBBE (*Ber.*, 1897, **30**, 94—97).—*Ethylic diphenylitaconate* was prepared by passing gaseous hydrogen chloride into a boiling alcoholic solution of the acid; it melts at 44—45°. When it is mixed with benzaldehyde and the mixture added gradually to alcoholic sodium ethoxide cooled to −18°, the sodium salt of *γ-diphenyl-α-benzylideneitaconic acid*,

$$COOH\cdot C(CHPh)\cdot C(CPh_2)\cdot COOH,$$

separates; this acid turns red when heated, and then melts at 207°; its *calcium salt* crystallises with $3H_2O$ and is very sparingly soluble in water.

Ethylic methylphenylitaconate boils at 305—307°; by condensation with benzil in the presence of sodium ethoxide it yields yellow *α-desylene-γ-phenylmethylitaconic acid*,

$$COOH\cdot C(CPh\cdot CPhO)\cdot C(CMePh)\cdot COOH,$$

melting at 227—230°, the *potassium* salt of which is white, anhydrous, and sparingly soluble. If a freshly-prepared ethereal solution of the acid is treated with piperidine, a piperidine salt, melting and decomposing at 100°, separates; if the ethereal solution has first been allowed to remain for a few days in the light, the piperidine salt which separates melts and decomposes at 200°; the original acid is regenerated from both of these salts, which are probably stereoisomeric.

γ-Phenylmethyl-α-isopropyleneitaconic acid,

$$COOH\cdot C(:CMe_2)\cdot C(:CMePh)\cdot COOH,$$

was obtained from ethylic phenylmethylitaconate and acetone; it melts and decomposes at 223°. C. F. B.

Action of Phenyl Iodosochloride on Mercury Diphenyl: Production of Phenyl Iodochloride and other Compounds.—By H. CONRAD C. WILLGERODT (*Ber.*, 1897, **30**, 56—58. Compare Abstr., 1895, i, 635.)—When mercury diphenyl and phenyl iodosochloride are agitated during 15 minutes with water, and finally heated until the water boils, diphenyliodinium chloride and phenylmercurichloride are formed, and the same products are obtained if the original compounds are agitated with water at the ordinary temperature during 4 hours. M. O. F.

Thiobenzophenone. By LUDWIG GATTERMANN and H. SCHULZE. (*Ber.*, 1897, **29**, 2944—2945).—It is not possible to obtain absolutely pure thiobenzophenone by the method previously described, namely, the action of phosphorus pentasulphide on benzophenone in benzene solution. A very pure product is, however, obtained if benzophenone chloride be treated with an alcoholic solution of potassium sulphide, prepared by saturating an alcoholic solution of potassium hydroxide with hydrogen sulphide. The thiobenzophenone thus obtained distils at 174° (14 mm.) as a fine, deep blue oil, which soon solidifies to long, blue needles. A sharp melting point cannot be observed, but the thioketone melts lower than benzophenone. With alcoholic potassium hydroxide, it is reconverted into benzophenone; with hydroxylamine, it gives benzophenoxime, and, on heating with copper oxide, it yields tetraphenylethylene. J. F. T.

Derivatives of Benzophenone. By PIETRO BARTOLOTTI (*Gazzetta*, 1896, **26**, ii, 433–441).—*Benzoylguaiacol* is formed with development of heat on adding benzoic chloride to a solution of guaiacol in soda; it forms white crystals, melting at 52—53°. When heated on the water bath with benzoic chloride and anhydrous zinc chloride, hydrogen chloride is evolved, and on treating the mass with water and sodium carbonate, a residue is obtained which yields lustrous, colourless crystals of *benzoylbenzoguaiacol*, $OMe\cdot C_6H_3Bz\cdot OBz$, melting at 95—96·5° after crystallisation, first from alcohol and subsequently from ethylic acetate and petroleum. On warming its alcoholic solution with alcoholic soda, and acidifying with sulphuric acid, *benzoguaiacol*, $OMe\cdot C_6H_3Bz\cdot OH$ [$OMe : OH = 1 : 2$], is obtained; it separates from alcohol in large, pale yellow crystals melting at 131—132°, and is constitutionally related to cotoïn and hydrocotoïn.

On warming a mixture of trimethylpyrogallol, benzoic chloride, and anhydrous zinc chloride on the water bath, hydrogen chloride is evolved, and after treating with water and sodium carbonate, and crystallising from dilute acetic acid, large yellow crystals of *benzopyrogallol dimethylic ether*, $C_6H_2Bz(OMe)_2\cdot OH$, [$(OMe)_2 : OH = 1 : 2 : 3$], melting at 130—131°, are obtained. It is isomeric with hydrocotoïn in which $(OMe)_2 : OH = 1 : 3 : 5$, and is accompanied by small quantities of *benzoylpyrogallol dimethylic ether*, $C_6H_3(OMe)_2\cdot OBz$, which crystallises in large, colourless prisms melting at 116—117°.

On determining the methoxyl present in benzoguaiacol and in benzopyrogallol dimethylic ether, by treating with hydriodic acid by Zeisel's method, two substances are obtained which are still under examination; they are probably the corresponding ketophenols.

W. J. P.

α-Amido-β-naphthylic Ethylic Ether. By LUDWIG PAUL (*Zeit. angw. Chem.*, 1896, 620—622).—Instructions are given for the manufacture of the ethylic ether of α-amido-β-naphthol. β-naphthol is first etherified, and the ether is then mixed with its own weight of water and treated with the requisite quantity of nitric acid (40°Bé.); the α-nitro-compound obtained in this way yields the α-amido-β-naphthylic ethylic ether on reduction with zinc dust and hydrochloric acid. On treating the amido-ether with acetic anhydride in benzene solution, it is converted into a *monacetyl derivative*, which crystallises in slender, colourless needles, and melts at 144°.

β-Naphthylic methylic ether, when nitrated, yields an α-nitro-derivative, which crystallises from alcohol in large, colourless plates, melts at 125·5°, and on reduction yields the corresponding amido-compound. These ethers of α-amido-β-naphthol can be used in the manufacture of dyes in place of α-naphthylamine. J. J. S.

Naphthacetol. By OTTO N. WITT and JENS DEDICHEN (*Ber.*, 1897, **29**, 2945—2954).—It is well known that the value of the azo-dyes derived from β-naphthol lies in the fact that the combination with the diazo-chloride takes place in the ortho-position relatively to the hydroxyl group, and that the compound thus formed retains only to a very slight extent the phenolic character of the parent substance. In α-naphthol, on the other hand, of the positions 2 and 4 in which the diazo-group can enter, preference is nearly always given to the position 4, and the dye formed is, therefore, strongly phenolic and basic in character, a fact which considerably affects its dyeing properties.

If, however, the diazo-group be made to combine in the ortho-position relatively to the hydroxyl, the dyes are then quite as fast to light as those derived from β-naphthol, and even surpass them in shade. This combination can be brought about by the presence of an inert group in the para-position in α-naphthol.

4-*Acetamido-α-naphthol* (parahydroxy-α-acetonaphthalide), $C_8H_6(OH)\cdot NHAc\ [=1:4]$, for which the name *naphthacetol* is proposed, is a substance which fulfils these conditions. It is best prepared by the method of Grandmougin and Michel by the acetylation of paramido-α-naphthol with acetic anhydride; it forms slender, white needles melting at 187° after recrystallisation from alcohol. Naphthacetol readily reacts with most diazo-compounds with the production of azo-compounds analogous to those derived from β-naphthol, but somewhat bluer in shade.

Benzeneazonaphthacetol is formed when an alcoholic solution of naphthacetol is treated with diazobenzene chloride; when recrystallised from pyridine, it forms red needles melting at 267—268°. On dissolving the dye in an alcoholic solution of potash, and adding the requisite quantity of methylic iodide, the *methylic ether* is obtained, a scarlet-red, crystalline substance melting at 218—220° after recrystallisation from xylene. The production of this methylic ether shows that the phenolic character of the hydroxyl-group is not quite destroyed.

Naphthacetol combines with diazosulphonic acids with the production of soluble dyes very similar to those derived from β-naphthol.

It does not appear possible to obtain the amido-derivative of naphthacetol by the reduction of the azo-dye; the compound is certainly formed, but decomposes on attempts being made to recrystallise it. It is readily converted into the corresponding *quinone* on treating its aqueous solution with excess of ferric chloride; the quinone separates from dilute alcohol in orange-red needles melting and decomposing at 220°. If the diazo-group has in reality entered in the ortho-position relatively to the hydroxyl-group, this compound must be a derivative of β-naphthaquinone; this was proved to be the case by the production of an *acetylphenonaphtheurhodine* by combining it with orthophenylenediamine in acetic acid solution. This compound crystallises from phenol or alcohol in lemon-yellow needles which do not melt at 360°; on treatment with concentrated hydrochloric acid, it yields blood-red needles of the hydrochloride of phenonaphtheurhodine, which can be converted into the eurhodine by treatment with ammonia. This eurhodine melts at 294°, and is in every respect identical with typical eurhodine. The production of hydroxynaphthaquinone and of acetyleurhodine, moreover, shows that the diazo-group has entered in the ortho-position relatively to the hydroxyl.

Naphthacetol, like β-naphthol, readily yields a *nitroso*-derivative, which crystallises from glacial acetic acid in golden needles melting at 203°.

By employing other acid anhydrides in the acidylation of paramido-α-naphthol, homologues of naphthacetol are produced. 4-*Butyramido-α-naphthol* crystallises from alcohol in colourless, flat needles melting at 160—161°. 4-*Valeramido-α-naphthol* forms colourless crystals melting at 204—205°. 4-*Benzamido-α-naphthol* separates from alcohol in glistening, white needles melting at 228—229°. This benzoyl derivative can also be prepared by the Baumann-Schotten method from the hydrochloride of amidonaphthol and benzoic chloride.

J. F. T.

1:1′-Dihydroxynaphthalene-4-sulphonic Acid. By Ludwig Paul (*Zeit. angw. Chem.*, 1896, 619—620).—To prepare 1:1′-dihydroxynaphthalene-4-sulphonic acid, α-naphthol-δ-disulphonic acid is fused with sodium hydroxide at 210—215° for some 2½ hours. Details are given for the manufacture of the acid on the large scale. J. J. S.

Colouring Matters Derived from the Sulphonic Acids of α-Naphthol and α-Naphthylamine. By Ludwig Gattermann and H. Schulze (*Ber.*, 1897, **30**, 50—55).—The two following laws have been established with regard to the production of azo-colouring matters from the sulphonic acids of α-naphthol and α-naphthylamine: 1. When the para-position with respect to the hydroxy- or amido-group is free, and the neighbouring positions in either benzene nucleus are not substituted by a sulphonic group, colouring matters of the para-series are obtained. 2. When substitution has occurred in the para-position, or the sulphonic radicle occupies either of the neighbouring positions, colouring matters of the ortho-series are formed, provided substitution in this position has not previously occurred.

The colouring matters obtained by the action of diazo-compounds on 1 : 4′-hydroxynaphthalenesulphonic, 1 : 4′-amidonaphthalenesulphonic, 1 : 3-hydroxynaphthalenesulphonic, 1 : 3-amidonaphthalenesulphonic, and 1 : 2 : 4′-hydroxynaphthalenedisulphonic acids have been studied from this point of view.

1 : 4′-Hydroxynaphthalenesulphonic acid, when dissolved in soda and treated with diazobenzene chloride, yields the *sodium* salt of 2-benzeneazo-1 : 4′-hydroxynaphthalenesulphonic acid, which crystallises from water in red leaflets; this colouring matter is known as cochineal scarlet G. Reduction with stannous chloride and hydrochloric acid gives rise to 2 : 1 : 4′-amidohydroxynaphthalenesulphonic acid, and this substance, on treatment with sodium amalgam, yields 2 : 1-amidohydroxynaphthalene, and not the 1 : 4-derivative.

1 : 4′-Amidonaphthalenesulphonic acid combines with diazobenzene, forming 2-benzeneazo-1 : 4′-amidonaphthalenesulphonic acid, the *sodium* salt crystallising from water in beautiful red leaflets; the *benzylidene* derivative is a white, crystalline substance, which resists the action of hydrochloric acid at 150°. Reduction with stannous chloride and hydrochloric acid gives rise to 1 : 2 : 4′-diamidonaphthalenesulphonic acid, which, on treatment with sodium amalgam, is converted into 1 : 2-naphthylenediamine.

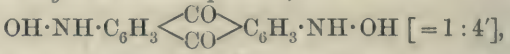
The *sodium* salt of 2-benzeneazo-1 : 3-naphthalenesulphonic acid is obtained from 1 : 3-naphthalenesulphonic acid and diazobenzene chloride, and crystallises from water in red leaflets resembling eosin; when reduced with stannous chloride, it yields 2 : 1 : 3-amidohydroxynaphthalenesulphonic acid, and this is converted into 2 : 1-amidohydroxynaphthalene under the influence of sodium amalgam.

1 : 3-Amidonaphthalenesulphonic acid does not combine with diazobenzene chloride, but the action of paranitrodiazobenzene chloride gives rise to a reddish-violet colouring matter, which yields 1 : 2 : 3-naphthylenediaminesulphonic acid on reduction; when this is reduced with sodium amalgam 1 : 2-naphthylenediamine is formed.

M. O. F.

Hydroxlyamine Derivatives of Anthraquinone. By ROBERT E. SCHMIDT and LUDWIG GATTERMANN (*Ber.*, 1897, **29**, 2934—2943).—In the reduction of nitro-anthraquinones to the corresponding amido-compounds by means of alkaline reducing agents, green to blue intermediate products are obtained, which are soluble in alkalis and are converted by further reduction into the amido-derivatives. These intermediate products are the hydroxylamine derivatives of anthraquinone, and are well defined crystalline substances which, on treatment with concentrated sulphuric acid, undergo intramolecular rearrangement, being converted into the corresponding amidohydroxyanthraquinones.

1 : 4′-*Dihydroxylamineanthraquinone*,



$$\mathrm{OH\cdot NH\cdot C_6H_3}{<}{}^{\mathrm{CO}}_{\mathrm{CO}}{>}\mathrm{C_6H_3\cdot NH\cdot OH}\ [=1:4'],$$

is obtained on reducing 1 : 4′-dinitroanthraquinone with stannous chloride and sodium hydroxide, the 1 : 4′-dinitroanthraquinone being the one which yields anthrarufin on reduction, diazotising the diamido-derivative thus formed, and heating the tetrazo-derivative with acids. The substance has no definite melting point, but the pure blue colour of its alkaline solution is characteristic. It dissolves in concentrated hydrochloric acid, forming a colourless solution, which, however, on dilution, yields the hydroxylamine compound again unchanged. By further reduction, it passes into 1 : 4′-diamidoanthraquinone. The *dibenzoyl* derivative, obtained by the action of 2 mols. of benzoic chloride on 1 mol. of the hydroxylamine compound, consists of garnet-red needles melting at 188°. In strong alkaline solutions, and employing an excess of benzoic chloride, the *tribenzoyl* derivative, an orange-yellow compound melting at 228°, can be obtained. On heating 1 : 4′-dihydroxylamineanthraquinone with concentrated sulphuric acid, it readily undergoes molecular rearrangement, with the production chiefly of two isomeric diamidodihydroxyanthraquinones, called respectively the α and β, together with a third, the γ, in somewhat smaller quantities. These can be separated from one another by taking advantage of their relative solubilities in dilute sulphuric acid, alkalis and acetone.

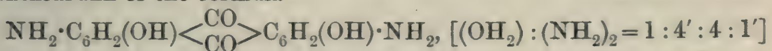
α-Diamidodihydroxyanthraquinone dissolves in hot nitrobenzene, forming a violet-blue solution, which, on cooling, deposits long, brassy needles; it dissolves in concentrated sulphuric acid, and the yellow solution, on the addition of boric acid, becomes blue, and then shows a sharp and characteristic absorption spectra.

β-Diamidodihydroxyanthraquinone crystallises from acetone in dark, metallic green crystals, which also give a characteristic absorption spectra when treated in the manner described above.

γ-Diamidodihydroxyanthraquinone, which is obtained only in small quantities, dissolves in sulphuric acid, forming a yellow solution which is not altered by adding boric acid to it. If, however, it is heated with a 10 per cent. solution of boric acid in concentrated sulphuric acid at 80—100°, a fine, bluish-red solution is obtained, having a cinnabar-red fluorescence, and showing a characteristic absorption band in the green.

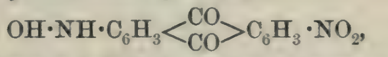
By the action of sulphur and fuming sulphuric acid at ordinary temperatures on 1 : 4′-dinitroanthraquinone, the chief products are the above-mentioned α-and β-diamidodihydroxyanthraquinones, together with a small quantity of a third substance, which is probably identical with the γ-compound ; at the same time, a fourth substance (δ) containing sulphur is produced.

On nitrating anthrarufin and subsequently reducing the dinitroderivative, a compound identical with the previously described α-diamidodihydroxyanthraquinone is formed ; this must be a diparamidoanthrarufin of the formula



$$NH_2{\cdot}C_6H_2(OH){<}\substack{CO\\CO}{>}C_6H_2(OH){\cdot}NH_2,\ [(OH_2):(NH_2)_2=1:4':4:1']$$

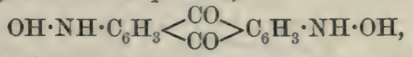
1 : 4′-*Nitrohydroxylamineanthraquinone,*



$$OH{\cdot}NH{\cdot}C_6H_3{<}\substack{CO\\CO}{>}C_6H_3{\cdot}NO_2,$$

is obtained on reducing 1:4′-dinitroanthraquinone with phenylhydrazine and alcohol ; it crystallises from acetone in long needles.

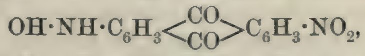
1 : 1′-*Dihydroxylamineanthraquinone,*



$$OH{\cdot}NH{\cdot}C_6H_3{<}\substack{CO\\CO}{>}C_6H_3{\cdot}NH{\cdot}OH,$$

is formed from 1 : 1′-dinitroanthraquinone, that is, the dinitroanthraquinone which, on reduction, &c., yields chrysazin ; the reduction is conducted in the same manner as in the case of the 1 : 4′ compound, its solution in alkalis is green.

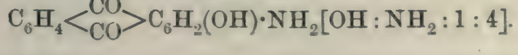
1:1′-*Nitrohydroxylamineanthraquinone,*



$$OH{\cdot}NH{\cdot}C_6H_3{<}\substack{CO\\CO}{>}C_6H_3{\cdot}NO_2,$$

is insoluble in a solution of sodium hydroxide ; it crystallises from pyridine and methylic alcohol in glistening crystals.

1:-*Hydroxylamineanthraquinone* is formed on reducing 1-nitroanthraquinone with the requisite quantity of stannous chloride and sodium hydroxide in aqueous alcoholic solution. It separates from acetone in fine, red-brown crystals which dissolve in a solution of sodium hydroxide, yielding a green solution. On treatment with concentrated sulphuric acid, it is transformed into an amidohydroxyanthraquinone, which, since it can be produced by the action of sulphur sesquioxide on the mononitroanthraquinone, as well as by the action of ammonia on quinizarin, must have the constitution



$$C_6H_4{<}\substack{CO\\CO}{>}C_6H_2(OH){\cdot}NH_2[OH:NH_2:1:4].$$

J. F. T.

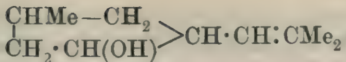
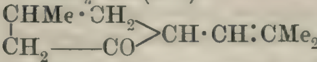
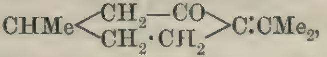
Oil of Roses. By Eugène Charabot and G. Chiris (*Compt. rend.*, 1896, **123**, 752—753).—In the examination of a large number of samples of rose-water, the authors have always observed the presence of a certain amount of acid (about 0·0003 gram per litre as acetic acid). This they regard as confirmatory of the statement made by Dupont and Guerlain (this vol., i, 160), to the effect that oil of roses contains an ether which is hydrolysed by prolonged boiling with water. If the primitive apparatus employed in the distillation of the oil in the East had been used, the authors are of opinion that they would have found larger amounts of acid than in the samples of rose-water with which they worked. A. C. C.

Artificial Production of Pulegone from Citronellaldehyde. By FERDINAND TIEMANN and R. SCHMIDT (*Ber.*, 1897, **30**, 22—32). —In view of the fact that pulegone yields acetone and methylcyclohexenone when heated with formic acid (Abstr., 1896, i, 309), the behaviour of isopulegone, obtained from isopulegol (Abstr., 1896, i, 383), towards this agent has been studied. Isopulegol is the alcohol obtained in the form of acetate when citronellaldehyde is heated with an equal weight of acetic anhydride under pressure, and on treating the corresponding ketone with formic acid, methylcyclohexenone is obtained, identical in every respect with the substance produced from pulegone; the identity, however, does not extend to the original ketones and alcohols, which exhibit certain differences among themselves. For instance, natural pulegone boils at 99—101° under a pressure of 12 mm., and forms a crystalline sodium hydrogen sulphite compound, whilst isopulegone boils at 90° under a pressure of 12 mm., and does not combine with sodium hydrogen sulphite; pulegol obtained from natural pulegone, and containing a small quantity of menthol, boils at 108—110° under a pressure of 14 mm., whilst isopulegol boils at 91° under a pressure of 13 mm. Moreover, natural pulegone and pulegol readily yield menthol when reduced with sodium and alcohol, whilst alcoholic solutions of isopulegone and isopulegol resist the action of the metal. Another difference between pulegone and isopulegone lies in their behaviour towards hydroxylamine, the former yielding a normal oxime, $C_{10}H_{17}NO$, which melts at 118—119°, and an oxime, $C_{10}H_{19}NO_2$, which melts at 147° (compare Beckmann and Pleissner, Abstr., 1891, 936); isopulegone forms two oximes, which have the same composition,

$$C_{10}H_{17}NO,$$

but melt at 120—121° and 134° respectively. Again, the semicarbazones of pulegone and isopulegone melt at 172° and 173° respectively, but they are not identical, as the crystals which separate from the mixed alcoholic solutions melt at a temperature considerably lower.

Isopulegone (Abstr., 1896, i, 383) in a 1 decimetre tube has $\alpha_D =$ + 10° 15′; the sp. gr. = 0·9213 at 17·5°, the refractive index $n_D = 1·4690$, and the molecular refraction $M = 45·98$. As already stated, it does not yield a compound with sodium hydrogen sulphite, and when treated with sodium and alcohol, is converted into isopulegol, no menthol being produced. When the ketone is agitated during 50—60 hours with 5 per cent barium hydroxide, however, it is completely converted into pulegone, which is also formed when isopulegone is allowed to remain in alcoholic solution with 5 per cent. barium hydroxide at ordinary temperatures.

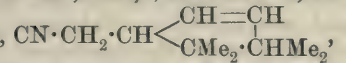
The authors suggest the possibility of representing isopulegol by the formula  $\left.\begin{array}{l}\mathrm{CHMe{-}CH_2}\\ \mathrm{\overset{|}{C}H_2{\cdot}CH(OH)}\end{array}\right>\mathrm{CH{\cdot}CH{:}CMe_2}$ ascribing to isopulegone the formula  $\left.\begin{array}{l}\mathrm{CHMe{\cdot}CH_2}\\ \mathrm{\overset{|}{C}H_2{-\!-\!-}CO}\end{array}\right>\mathrm{CH{\cdot}CH{:}CMe_2}$; this explanation of the isomerism however, involves the conversion of the last-named substance into pulegone,  $\mathrm{CHMe}\left<\begin{array}{l}\mathrm{CH_2{-}CO}\\ \mathrm{CH_2{\cdot}CH_2}\end{array}\right>\mathrm{C{:}CMe_2}$, under the influence of barium hydroxide. M. O. F.

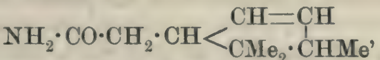
Dextro and Lævo Configurations in the Citronellal Series. By Ferdinand Tiemann and R. Schmidt (*Ber.*, 1896, **30**, 33—38).—It has been shown that, whilst citronellaldehyde, citronellol, citronellic acid, and the β-methyladipic acid, to which they give rise on oxidation, are dextro-rotatory, rhodinol, from Turkish rose oil, constitutes the citronellol of the lævo-gyrate series; other members of both groups have now been obtained.

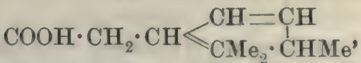
The *semicarbazone* of *d*-citronellaldehyde crystallises in leaflets, and melts at 82·5°. The nitrile of *d*-citronellic acid boils at 104—106° under a pressure of 14 mm. (compare Semmler, Abstr., 1893, i, 685).

By the oxidation of *l*-citronellol (from rose oil), a small quantity of *l*-citronellaldehyde has been obtained, along with *l-citronellic acid*, which boils at 143—144°, under a pressure of 14 mm., has, in a 1 decimetre tube, $a_D = -6° 15'$, and the refractive index $n_D = 1·4536$ at 20°; the *silver* salt is unstable, and does not dissolve in water. Citronellic acid, obtained from Reunion geranium oil, is a mixture of *d*- and *l*-citronellic acids.

Menthone is not produced when Reunion geranium oil (pelargonium oil) is oxidised, as stated by Barbier and Bouveault; the ketone obtained from this source is isopulegone. M. O. F.

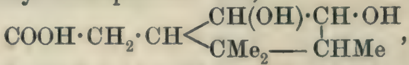
Camphor. By J. C. W. Ferdinand Tiemann (*Ber.*, 1897, **30**, 242—265. Compare Abstr., 1895, i, 426 and 675; also this vol., i, 161).—β-Campholenonitrile,  $\mathrm{CN{\cdot}CH_2{\cdot}CH}\left<\begin{array}{l}\mathrm{CH{=}CH}\\ \mathrm{CMe_2{\cdot}\overset{|}{C}HMe_2}\end{array}\right.$, is obtained when the dehydration of camphoroxime is effected by the agency of concentrated acids, isoamidocamphor, β-campholenamide, and dihydrocampholenolactone being also produced; it is optically inactive, boils at 225°, and has the odour of the α-modification. Reduction in alcoholic solution with sodium gives rise to β-camphylamine, which is optically inactive, and boils at 196—198°.

β-Campholenamide,  $\mathrm{NH_2{\cdot}CO{\cdot}CH_2{\cdot}CH}\left<\begin{array}{l}\mathrm{CH{=}CH}\\ \mathrm{CMe_2{\cdot}\overset{|}{C}HMe}\end{array}\right.$, is produced on hydrolysing the β-nitrile with alcoholic potash, and is also formed when ammonium β-campholenate is heated in sealed tubes at temperatures above 200° during several hours; an aqueous solution of isoamidocamphor hydrochloride also yields β-campholenamide when boiled; it crystallises in long, colourless needles, melts at 86°, and is optically inactive.

β-Campholenic acid,  $\mathrm{COOH{\cdot}CH_2{\cdot}CH}\left<\begin{array}{l}\mathrm{CH{=}CH}\\ \mathrm{CMe_2{\cdot}\overset{|}{C}HMe}\end{array}\right.$, is obtained by hydrolysing the nitrile, or amide, with alcoholic potash, and melts at

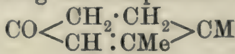
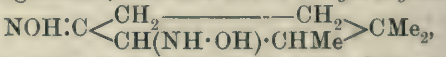
52°, boiling under atmospheric pressure at 245°; the *ammonium* salt crystallises in small prisms and melts at 130°; the *calcium* salt forms slender needles, and the *ethylic* salt is a colourless, optically inactive oil which boils at 222—225° under atmospheric pressure.

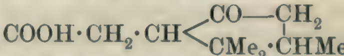
β-Dihydroxydihydrocampholenic acid,



$$\mathrm{COOH\cdot CH_2\cdot CH}<\begin{matrix}\mathrm{CH(OH)\cdot CH\cdot OH}\\ \mathrm{CMe_2—CHMe}\end{matrix},$$

is formed when β-campholenic acid is oxidised with potassium permanganate; it crystallises from chloroform or water in slender, lustrous needles, and melts at 146°. The acid sublimes under atmospheric pressure without undergoing decomposition, whilst the α-modification yields water and *l*-pinonic acid. 3 : 4 : 4-*Trimethylheptan-2-oldioic acid*, $\mathrm{COOH\cdot CH_2\cdot CH_2\cdot CMe_2\cdot CHMe\cdot CH(OH)\cdot COOH}$, is also a product of the action of potassium permanganate on β-campholenic acid; the substance is an unstable syrup, and when distilled under atmospheric pressure, or in a current of steam, it yields an unsaturated cyclic ketone, isocamphorone, having the composition $C_9H_{14}O$.

Isocamphorone,  $\mathrm{CO}<\begin{matrix}\mathrm{CH_2\cdot CH_2}\\ \mathrm{CH:CMe}\end{matrix}>\mathrm{CMe_2}$, is obtained by concentrating the liquid produced on oxidising β-campholenic acid with potassium permanganate, acidifying with sulphuric acid, and distilling the product in an atmosphere of steam; it boils at 97—99° under a pressure of 13 mm., and at 217° under atmospheric pressure. The ketone has the odour of camphorone, with which it is isomeric; the sp. gr. = 0·9424 at 20°, and the refractive index $n_D = 1·48458$, whence the molecular refraction, M = 41·93. The *semicarbazone* crystallises from ethylic acetate in long needles, and melts at 211°. *Hydroxylamidodihydrocamphorone oxime*,  $\mathrm{NOH:C}<\begin{matrix}\mathrm{CH_2——CH_2}\\ \mathrm{CH(NH\cdot OH)\cdot CHMe}\end{matrix}>\mathrm{CMe_2}$, is obtained by the action of alcoholic hydroxylamine on the ketone, being produced when the latter is present in excess; it separates in large, lustrous crystals and melts at 153°. Fehling's solution is at once reduced by an alcoholic solution of the substance.

Campholonic acid,  $\mathrm{COOH\cdot CH_2\cdot CH}<\begin{matrix}\mathrm{CO—CH_2}\\ \mathrm{CMe_2\cdot CHMe}\end{matrix}$, remains in the acid liquid after removing isocamphorone by means of a current of steam; it has not been hitherto obtained in crystalline form, but the *sodium* salt crystallises readily, and the *semicarbazone* melts at 224°. Campholonic acid is isomeric with the pinonic acids, but, on treatment with sulphuric acid, yields a ketone which is probably dihydroisocamphorone; the pinonic acids give rise to methoethylheptanonolide.

3-*Dimethylhexan-2-onoic acid* (acetyldimethylbutyric acid),

$$\mathrm{COMe\cdot CMe_2\cdot CH_2\cdot CH_2\cdot COOH},$$

is produced on oxidising β-dihydroxydihydrocampholenic acid with chromic acid (Abstr., 1895, i, 677), and crystallises from water in lustrous prisms; it melts at 48°, and boils at 150°, 160·5°, and 178° under pressures of 10 mm., 13 mm., and 20 mm. respectively. The *ammonium* salt melts at 110°, and the *semicarbazone* at 185°; the acid is also formed when isocamphorone is oxidised with potassium permanganate. When the oxidation of β-dihydroxydihydrocampholenic acid is effected with a considerable quantity of chromic acid, asymmetric α-dimethylglutaric acid (m. p. 85°) is produced; dimethylglutaric acid is also obtained on oxidising isocamphorone.

Although mineral acids convert β-campholenic acid into dihydrocampholenolactone, nitric acid oxidises a portion of the substance before the lactone is produced (compare Abstr., 1896, i, 55); volatile, fatty acids, asymmetric α-dimethylglutaric and dimethylsuccinic acids are obtained in this way, along with isocamphoronic acid.

A discussion of the constitution of β-campholenic derivatives, and their products of change, follows the experimental details.

M. O. F.

Action of Aluminium Chloride on Camphoric Anhydride. By G. Blanc (*Compt. rend.*, 1896, **123**, 749—752).—In investigating the action of aluminium chloride on camphoric anhydride dissolved in benzene, Bürcker obtained a condensation product of the two substances with disengagement of carbonic oxide (Abstr., 1896, i, 179). The author has studied the action of aluminium chloride on the anhydride in the presence of an inert solvent—chloroform. The product of the action, which was attended with evolution of carbonic oxide and hydrogen chloride, was an acid of the formula $C_9H_{14}O_2$. From dilute alcohol, it separates in colourless crystals melting at 132—133° and boiling at 247—249°; it dissolves readily in all the ordinary organic solvents. The salts of sodium, potassium, calcium, and barium are soluble in water, those of lead, zinc, copper, and cobalt are insoluble in water, but readily soluble in ether. The following ethereal salts were prepared by Meyer's method. All are liquids. *Methylic* salt, boiling at 203—204°. *Ethylic* salt, boiling at 214°. *Normal propylic* salt, boiling at 233—235°. *Isobutylic* salt, boiling at 241—243°. They are easily hydrolysed by alcoholic potash and by concentrated sulphuric acid. By treating the acid with phosphorus pentachloride and fractionating under reduced pressure, the *acid chloride*, $C_9H_{13}OCl$, was obtained as a mobile liquid boiling at 100—102° (40 mm.), and with decomposition at 212—214° under 760 mm. pressure. Ammonia, aniline, and phenylhydrazine react with this substance in ethereal solution, yielding the amide, anilide, and phenylhydrazide respectively. The *amide*, $C_9H_{13}O\cdot NH_2$, consists of fine, monoclinic crystals melting at 129—130°; it is readily soluble in alcohol, but only slightly so in light petroleum. The *anilide*, $C_9H_{13}O\cdot NHPh$, melts at 104°. The *phenylhydrazide*, $C_9H_{13}O\cdot N_2H_2Ph$, occurs as slender, monoclinic crystals melting at 130°. These three compounds are neither hydrolysed by alcoholic potash nor by sulphuric acid. The author is endeavouring to determine the constitution of the acid $C_9H_{14}O_2$. A. C. C.

Onocerin. By Hermann Thoms (*Ber.*, 1896, **29**, 2985—2991).—The roots of *Ononis spinosa L.* yield the glucoside ononin and a substance to which Hlasiwetz has given the name onocerin (*J. pr. Chem.*, 1855, **65**, 419); the latter compound has now been investigated by the author, who regards it as a dihydric secondary alcohol of the composition $C_{26}H_{44}O_2$.

Onocol (onocerin) is obtained by extracting the roots with 90 per cent. alcohol, and treating with 60 per cent. alcohol the residue obtained on evaporating the extract; onocerin remains undissolved, and is recrystallised from absolute alcohol, from which it separates in colourless, microscopic prisms. The substance dissolves with difficulty in ethylic acetate, ether, and chloroform; it melts at 232°. The *diacetyl* derivative is crystalline, and melts at 224°; the *dibenzoyl* derivative melts at 175—190°. On adding bromine to a solution of the diacetyl derivative in glacial acetic acid, the *tetrabromide* is produced; it melts and decomposes at 140—145°.

Onoketone, $C_{26}H_{40}O_2$, is obtained by dissolving onocerin in glacial acetic acid and adding powdered potassium dichromate to the solution at 60°; it crystallises from alcohol in colourless needles, and melts at 186—187°. The *oxime* is a white, amorphous substance, and the *phenylhydrazone* is also amorphous; the *semicarbazone* melts and decomposes at 175°.

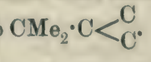
Oxidation of onoketone with chromic acid in glacial acetic acid gives rise to the *acid*, $C_{20}H_{30}O_5$, which melts at 75—80°, and appears to be related to abietic or pimaric acids; acetic and butyric acids appear to be produced when aqueous chromic acid is used.

The similarity between onocol and cholesterol leads the author to regard the former alcohol as belonging to the same class (compare Abstr., 1896, i, 425).

M. O. F.

Filicic Acid. By Girolamo Daccomo (*Gazzetta*, 1896, **26**, ii, 441—451).—On boiling a benzene solution of filicic acid with alcoholic hydroxylamine hydrochloride and calcium carbonate for several hours, filtering, distilling off the solvent, and treating with alkali, a residue is obtained which crystallises from alcohol in microscopic, reddish prisms melting at 150° with previous discoloration; it is soluble in alcohol or ether, has an odour of pyridine, and is the *anhydride* of the oxime of filicic acid, $C_{14}H_{15}O_4N$. The alkaline mother liquor obtained during its preparation gives a reddish precipitate with hydrochloric acid, but no pure product could be isolated from it.

By substituting ethylic acetate for benzene in the previous preparation, an *isomeride* of the above anhydride is obtained in microscopic, yellow prisms which melt at 197—198° with previous discoloration.

Copper filicate (Abstr., 1895, i, 68) is slowly converted into cuprous oxide by baryta water, and the liquor on distillation yields acetone, isobutyric acid, butyric acid, dimethylmalonic acid, and carbonic anhydride. This behaviour indicates that filicic acid is an aliphatic ketaldehyde containing the group  $CMe_2\cdot C<^{C}_{C}$.

W. J. P.

The Chemistry of Chlorophyll. By Leo Marchlewski (*J. pr. Chem.*, 1896, [2], **54**, 422—428.)—A reply to Tschirch (Abstr., 1896, i, 624).

J. F. T.

Hyposantonous Acid and its Decomposition Products. By Giuseppe Grassi-Cristàldi (*Gazzetta*, 1896, **26**, ii, 451—465).—The same hyposantonous acid is obtained by reducing either hyposantonin or isohyposantonin with zinc dust in acetic acid solution; it has the specific rotation $[\alpha]_D = +75{\cdot}95°$ (compare Andreocci, Abstr., 1896, i, 182). The *barium* salt crystallises with $2H_2O$, and the *silver* salt is a white powder; the *methylic* salt, $C_{15}H_{19}O_2Me$, crystallises in lustrous prisms melting at 43°, and has the specific rotation $[\alpha]_D = +79.14°$ at 28° in a 6 per cent. methylic alcohol solution.

On heating hyposantonous acid under reduced pressure at 350° with aqueous potash, propionic acid is formed, hydrogen is evolved, and an oil consisting of a mixture of dimethyldihydronaphthalene and 1 : 4-dimethylnaphthalene distils; the mixture is converted into pure 1 : 4-dimethylnaphthalene by heating with iodine. The hydrocarbon thus obtained is identical with that prepared by Cannizzaro and Andreocci (Abstr., 1896, i, 488); its formation from hyposantonous acid confirms Cannizzaro's view respecting the formation of 1 : 4-dimethylnaphthol, and is not in accordance with Klein's opinion (Abstr., 1894, i, 51) respecting the decomposition of santonous acid. W. J. P.

Coal-tar Bases. By Felix B. Ahrens (*Ber.*, 1896, **29**, 2996—2999. Compare Abstr., 1895, i, 390).—3 : 4-*Dimethylpyridine* (lutidine) has been isolated from the fraction of coal-tar light oil (*loc. cit.*) boiling at 164—165°, which is treated in acidic solution with mercuric chloride (3 mols.); it boils at 163·5—164·5°, and the odour is not disagreeable.

The *hydrochloride*, *hydrobromide*, and *hydriodide* crystallise in needles, and the *platinochloride*, which contains $2H_2O$, melts and decomposes at 205°; the *mercurichloride* crystallises in slender needles, and the *aurochloride* and *picrate* melt at 160—162° and 163° respectively. On oxidising the base with neutral potassium permanganate, 3 : 4-pyridinedicarboxylic (cinchomeronic) acid is produced.

2 : 4 : 5-*Trimethylpyridine* (collidine) is obtained in the form of an oily mercurichloride in isolating the foregoing base, and is purified by conversion into the picrate; it has a spice-like odour, and boils at 165—168°. The *platinochloride* contains $2H_2O$, which is eliminated at 100°, and melts at 205°, and effervesces vigorously; the *mercurichloride*, *aurochloride*, and *picrate* melt at 164—175°, 129—131°, and 128—131°, respectively. Oxidation with potassium permanganate converts the base into 2 : 4 : 5-pyridinetricarboxylic (berberonic) acid.

M. O. F.

Decomposition of Pipecolinic Acid into its two Optical Components. By Fritz Mende (*Ber.*, 1896, **29**, 2887—2889).—2-Methylpyridine was oxidised with potassium permanganate, and the 2-carboxylic acid formed was reduced, in boiling alcoholic solution, with sodium. The hot alcoholic solution of the pipecolinic acid thus obtained was heated with just more than enough *d*-tartaric acid to form a hydrogen tartrate with half of it. The *d-hydrogen tartrate* of *d-pipecolinic acid* separated from the cooled solution. This melts at 187°, and, after successive treatment with lead acetate and hydrogen sulphide, yields *d-pipecolinic acid*, which has, in a tube 100 mm. long and at 25°, a rotation varying from +3·63° in a solution of 9·92 per cent. concentration to +7·006° in one of 19·93 per cent.

When the mother liquor from the above-mentioned tartrate was treated successively with lead acetate and hydrogen sulphide, and *l*-tartaric acid added, the *l-hydrogen tartrate* of *l-pipecolinic acid* separated. This exactly resembles the isomeric compound, and, in like manner, the *l-pipecolinic acid* prepared from it resembles *d*-pipecolinic acid, except that its rotation is to the left ($-3{\cdot}54°$ in a solution of 9·92 per cent. concentration). C. F. B.

Action of Sulphur Bromide on Aromatic Amines. By ALBERT EDINGER (*J. pr. Chem.*, 1896, [2], **54**, 355—358).—The main facts in this paper have already appeared. (Compare this vol., i, 103). J. F. T.

Action of Sulphur Chloride on Quinoline. By ALBERT EDINGER and HANS LUBBERGER (*J. pr. Chem.*, 1896, [2], **54**, 340—358).—The main facts in this paper have already appeared. (Compare this vol., i, 103). J. F. T.

1-Hydroxyquinoline-4-sulphonic Acid and its Derivatives. By ADOLPH CLAUS and ROBERT GIWARTOVSKY (*J. pr. Chem.*, 1896, [2], **54**, 377—391).—1-Hydroxyquinoline-4-sulphonic acid, when brominated, gives rise to 2-*bromo*-1-*hydroxyquinoline*-4-*sulphonic acid* only, the position of the bromine atom being ascertained by its oxidation to quinolinic acid melting at 180°, and the formation from this of nicotinic acid melting at 228°, and also from its yielding 4-bromo-1-hydroxyquinoline (m. p. 124°) when boiled with sulphuric acid.

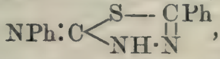
2-*Bromo*-1-*hydroxyquinoline* sublimes in long, colourless needles melting at 138°.

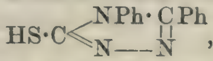
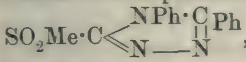
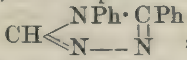
2-Bromo-1-hydroxyquinoline-4-sulphonic acid crystallises with $\frac{1}{2}H_2O$, from boiling water or hydrochloric acid; its salts, both normal and basic, are soluble in water.

The unbrominated hydroxysulphonic acid, after treatment for 24 hours with tin and hydrochloric acid, is completely reduced to tetrahydroquinoline-4-sulphonic acid, and the bromo-compound, when treated in the same way, yields tetrahydro-1-hydroxyquinoline-4-sulphonic acid, which is further reduced to tetrahydroquinoline-4-sulphonic acid, melting at 315°, if the reducing agent is allowed to act twice as long.

2-*Chloro*-1-*hydroxyquinoline*-4-*sulphonic acid* is best obtained by the action of chlorine on a solution of the sulphonic acid in hydrochloric acid, the product being mixed with a small quantity of 2 : 4-*dichloro*-1-*hydroxyquinoline*, which crystallises from alcohol in colourless needles melting at 179°. The pure chlorhydroxyquinolinesulphonic acid crystallises from its aqueous alcoholic solution in colourless needles and prisms containing $1H_2O$. Like the bromo-compound, it yields pyridinedicarboxylic acid and nicotinic acid on oxidation with potassium permanganate, thus proving the position of the chlorine atom. On treatment with sulphuric acid, the sulphonic acid group is eliminated, and 2-*chloro*-1-*hydroxyquinoline*, a compound crystallising in colourless needles and melting at 145°, is produced.

By the action of phosphorus pentachloride on 1-hydroxyquinoline-4-sulphonic acid, the sulphonic acid group is readily replaced by the halogen with the production of Hebebrand's 4-chloro-1-hydroxyquinoline melting at 125°, whilst phosphorus pentabromide gives rise to 2 : 4 : 3′-tribromo-1-hydroxyquinoline melting at 170°. It was not found possible to obtain the corresponding trichloro-derivative by this means; by prolonging the action of the pentachloride, other products were formed which are still under investigation. J. F. T.

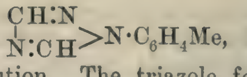
1-Benzoyl-4-phenylthiosemicarbazide. By WILHELM MARCKWALD and AUG. BOTT (*Ber.*, 1896, **29**, 2914—2920).—1-*Benzoyl-4-phenylthiosemicarbazide*, NHPh·CS·NH·NHBz, cannot be obtained by the action of benzoic chloride on phenylthiosemicarbazide, but is formed when phenylcarbimide and benzhydrazide are brought together in alcoholic solution. It forms white crystals, and melts at 162°. When treated with acetic chloride, it is converted into diphenylimidothiobiazoline,  $\mathrm{NPh{:}C}<\begin{array}{l}\mathrm{S-CPh}\\ \quad\;\;\|\\ \mathrm{NH\cdot N}\end{array}$, which is identical with a product previously obtained by Pulvermacher (Abstr., 1894, i, 304), by the action of benzoic chloride on phenylthiosemicarbazide. It has basic properties, and forms a sparingly soluble *hydrochloride* and *platinochloride*. The *acetyl* derivative melts at 140°. The base also forms a *nitroso*-compound, $C_{14}H_{10}N_4SO$, which crystallises in slender, yellowish-red needles.

When benzoylphenylthiosemicarbazide is treated with benzoic chloride, it again loses the elements of water, but forms diphenylimidobiazolyl mercaptan,  $\mathrm{HS\cdot C}<\begin{array}{l}\mathrm{NPh\cdot CPh}\\ \qquad\;\;\|\\ \mathrm{N-\!\!-\!\!-N}\end{array}$, which was also obtained by Pulvermacher, and is formed when benzoylphenylthiosemicarbazide is heated above its melting point. The *methiodide*, $C_{14}H_{11}N_3S,MeI$, forms white crystals, and when treated with alkalis yields the *base* $C_{15}H_{13}N_3S$, which crystallises in white needles melting at 164°. The *hydrochloride* melts at 161°, and the *sulphate* at about 250°, both salts being sparingly soluble in water. The *platinochloride* is a crystalline precipitate, and the *picrate* melts at 137°. The base is converted by oxidation with potassium permanganate into the corresponding *sulphone*,  $\mathrm{SO_2Me\cdot C}<\begin{array}{l}\mathrm{NPh\cdot CPh}\\ \qquad\;\;\|\\ \mathrm{N-\!\!-\!\!-N}\end{array}$, which crystallises in matted needles melting at 176°. This proves that the methylated compound is a sulphide, and the original substance a mercaptan. When the latter is heated with dilute nitric acid, the sulphur is removed as sulphuric acid and *diphenylimidobiazole*,  $\mathrm{CH}<\begin{array}{l}\mathrm{NPh\cdot CPh}\\ \qquad\;\;\|\\ \mathrm{N-\!\!-\!\!-N}\end{array}$, is formed; this melts at 142°. The *platinochloride* decomposes at about 160°, and the *picrate* melts at 174°.

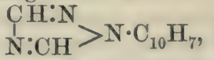
A. H.

Identity of Formopyrine and Methylenebiantipyrine. By GUIDO PELLIZZARI (*Gazzetta*, 1896, **26**, ii, 407—412).—The author shows, by chemical and crystallographical comparisons, that Marcourt's formopyrin (*Bull. Soc. Chim.*, [3], **15**, 520) is identical with his own methylenebiantipyrine (Abstr., 1890, 645).

W. J. P.

Monosubstituted Triazoles. By GUIDO PELLIZZARI and C. MASSA (*Gazzetta*, 1896, **26**, ii, 413—429).—Formylparatolylhydrazide gradually separates from a solution of tolylhydrazine in ethylic formate (compare Ruhemann, Trans., 1890, 50). On slowly heating its hydrochloride with formamide to 200°, ammonia and water are evolved, and the residue, after treatment with potash solution, is extracted with ether; a good yield of 1-*paratolyltriazole*,  $\begin{array}{l}\mathrm{CH{:}N}\\ \mathrm{N{:}CH}\end{array}\!\!>\mathrm{N{\cdot}C_6H_4Me}$, is obtained on evaporating the ethereal solution. The triazole forms a white, crystalline mass, which melts at 67° and boils at 265°; it is volatile in a current of steam, has an odour of pyridine, and is soluble in ether, alcohol, benzene, or chloroform, but insoluble in water. It is also obtained on distilling a mixture of the formyltolylhydrazide with formamide. The *platinochloride*, $(C_9H_9N_3)_2,H_2PtCl_6$, crystallises in yellow needles, and when boiled with water or heated at 150—175°, yields *tetrachloroplatoparatolyltriazole*, $(C_9H_9N_3)_2,PtCl_4$, as an insoluble, yellow powder; when heated at 175—200°, it seems to give *dichloroplatoparatolyltriazole*, $(C_9H_7N_3)_2PtCl_2$, but this substance could not be obtained pure.

1-*Orthotolyltriazole*, prepared in a similar manner from orthotolylhydrazide hydrochloride, is a colourless substance which melts at 45°, boils at 270°, and resembles its para-isomeride. The *platinochloride* crystallises in yellow needles, and on boiling with water or heating at 150—180°, is converted into *tetrachloroplatorthotolyltriazole*; it decomposes on prolonged heating at 200°.

1 : *α-Naphthyltriazole*,  $\begin{array}{l}\mathrm{CH{:}N}\\ \mathrm{N{:}CH}\end{array}\!\!>\mathrm{N{\cdot}C_{10}H_7}$, is prepared by gradually heating a mixture of α-naphthylhydrazide hydrochloride with formamide to 200°; formyl-α-naphthylhydrazide is formed as an intermediate product. The triazole crystallises from boiling water in lustrous, white needles, melting at 99°; it is odourless, and soluble in alcohol or chloroform. The *platinochloride*, $(C_{12}H_9N_3)_2,H_2PtCl_6$, forms small, yellow crystals, and on boiling with water, or heating at 160°, yields *tetrachloroplato-α-naphthyltriazole*, $(C_{12}H_9N_3)_2PtCl_4$, as a yellow, insoluble powder; on further heating, it is probably converted into the dichloro-compound by loss of 2HCl, but the product could not be purified.

1 : *β-Naphthyltriazole*, prepared by heating β-naphthylhydrazide hydrochloride with formamide at 120—150°, forms white crystals melting at 111°, and is rather more basic in properties than the preceding triazoles. The *platinochloride* crystallises in yellow needles and yields *tetrachloroplato-β-naphthyltriazole* as an insoluble, yellow powder when boiled with water or heated at 160—175°.

Orthotriazolebenzoic acid, $\begin{array}{l}\mathrm{CH{:}N}\\ \mathrm{N{:}CH}\end{array}\!\!>\mathrm{N{\cdot}C_6H_4{\cdot}COOH}$, is prepared by oxidising orthotolyltriazole with alkaline permanganate at 100°; after separating the manganese dioxide, it is precipitated by sulphuric acid and crystallises from alcohol in minute, white crystals melting at 264°. It is soluble in hot alcohol, but nearly insoluble in hot water; the *barium* salt $(C_9H_9N_3O_2)_2Ba$, is very soluble in water, whilst the *copper* salt is blue and insoluble.

Paratriazolebenzoic acid is prepared in like manner, and forms minute crystals which do not melt at 270°; the *barium* salt is sparingly soluble. W. J. P.

The Proteids of the Kidney Bean (Phaseolus vulgaris). By Thomas B. Osborne (*J. Amer. Chem. Soc.*, 1894, 16, 757—764. Compare Abstr., 1895, i, 454).—Phaseolin (*loc. cit.*) probably forms about 20 per cent. of the seed, the mean of 24 analyses gives the percentage composition as C = 52·58, H = 6·84, N = 16·47, S = 0·56, and O = 23·55.

Phaselin (*loc. cit.*) is slowly coagulated by heat at temperatures varying with the amount of salts present, and with the rapidity of heating. It is precipitated by acids; on prolonged dialysis yields insoluble or albuminate modifications, and has more nearly the properties of a globulin than of any other class of proteids. Its percentage composition (mean of 11 determinations) is C = 51·6, H = 7·02, N = 14·65, S = 0·49, and O = 26·24.

A small amount of *proteose* was also found in the extract.

J. J. S.

Hydrochloric Acid Compounds of Albumoses and Peptone. By OTTO COHNHEIM (*Zeit. Biol.*, 1896, **33**, 489—520).—The various albumoses and peptone differ from one another in the amount of hydrochloric acid with which they combine. In a 2·5 per cent. solution, they unite with hydrochloric acid, in percentages of their own weight, as follows: proto-albumose, 4·3; dentero-albumose, 5·5; hetero-albumose, 8·2; and antipeptone, 16 per cent. The proportion does not correspond exactly to any of the known properties of these substances, such as diffusibility, precipitability, &c. Probably the albumoses unite in different ways with the acid, some being more basic than others.

W. D. H.

Carbohydrate Group in the Albumin Molecule. By N. KRAWKOFF (*Pflüger's Archiv.*, 1896, **65**, 281—298).—Egg-albumin is freed with difficulty from ovo-mucoid, but the purest specimens obtained always yielded, after treatment with mineral acid, a reducing substance which gives with phenylhydrazine a crystalline osazone melting at 183—185° (Pavy gives 189—190°). The exact nature of this carbohydrate is not yet determined, but the main fact of its existence confirms the recent work of Pavy. No evidence, however, was found that artificial digestion of proteid leads to its appearance. Acid-albumin, alkali-albumin, commercial peptone, fibrin, serum-albumin, serum-globulin (slightly), lact-albumin (in traces) yield the same material. Casein, gelatin, vitellin, and nucleo-proteids from peas gave a negative result. Albumin from peas yielded an osazone with rather different characters.

W. D. H.

Chemical Structure of Hæmin and Hæmatin prepared by various methods. By M. BIALOBRZESKI (*Ber.*, 1896, **29**, 2842—2851).—The author confirms the formula

$$(C_{32}H_{31}N_4FeO_3Cl)_4,C_5H_{12}O,$$

given by Nencki and Sieber (Abstr., 1885, 70, 825) for the crystals of hæmin deposited from amylic alcohol. The mother liquors from the crystals obtained from the blood of horses by Nencki and Sieber's method give a mixture of substances partially soluble in ether; the soluble portion, which is an amorphous violet mass, dissolves readily in chloroform, alcohol, and alkalis, whilst the insoluble part is distinguished from hæmin by its greater stability towards nitric acid. Both portions, when dissolved in chloroform, give absorption spectra identical with that shown by hæmin in acid solution, but contain a higher percentage of carbon and hydrogen, the portion soluble in ether being somewhat poorer in iron content.

Hæmatin is readily obtained from the crystalline hæmin by treating it with a cold 10 per cent. solution of sodium hydroxide or by prolonged boiling with water; its composition is represented by the formula $C_{32}H_{31}N_4FeO_3$.

The method used by Schalféeff (Abstr., 1885, 566) for the isolation of hæmin is a very productive one; the crystalline hæmin, finally obtained, contains acetic acid after desiccation over sulphuric acid, and its composition is best represented by the formula

$$(C_{32}H_{31}N_4FeO_3Cl)_3,C_{32}H_{31}FeN_4O_3\cdot OAc,HOAc,$$

whether obtained from the blood of horses, oxen, or dogs. When it is hydrolysed with boiling water, no acetic acid is liberated, but sodium acetate is obtained if the hydrolysis be effected by means of dilute soda. The substance yields hæmatoporphyrin on treatment with hydrogen bromide, and has the composition $C_{16}H_{18}N_2O_3,HCl$.

Hæmin, obtained by either of the foregoing methods, contains no appreciable quantity of xanthine; it is certain, therefore, that the iron content is to that of nitrogen in the ratio of one atom of the former to four of the latter, hence its formula cannot be that proposed by Cloetta. When treated with cold sulphuric acid or alcoholic hydrogen chloride, it loses both nitrogen and iron, and gradually alters in character, assuming the properties described by Cloetta, and becoming insoluble in alkali; the ratio of the nitrogen to iron, however, remains approximately constant. This behaviour does not appear to be due to the presence of a labile aldehyde group, as phenylhydrazine has no action on the substance.

Cloetta's hæmin is separable into two approximately equal parts by dissolving it in chloroform and subsequently precipitating with ether; the composition of the two portions is different, and it is probable that we are here dealing with decomposition products of hæmin, for if the mother liquors obtained in preparing the substance by Cloetta's method be extracted with chloroform, the residual aqueous solution, on spectroscopic examination, will reveal the presence of hæmatoporphyrin. It is clear, therefore, that Cloetta's process induces an undesirable decomposition of the hæmin, the product containing too little nitrogen and iron.

A. L.

Phrenosin. By ALBRECHT C. L. M. L. KOSSEL (*J. pr. Chem.*, 1896, [2], 54, 215—216).—A reply to Thudichum (Abstr., 1896, i, 400).

A. G. B.

Organic Chemistry.

Preparation of Cyanamide. By REINHOLD WALTHER (*J. pr. Chem.*, 1896, [2], 510—512.)—A solution of cyanamide may be prepared very easily by dissolving thiocarbamide in 10 or 20 per cent. aqueous potassium hydroxide, adding gradually a 30 per cent. lead acetate solution, and finally filtering from the precipitated lead sulphide; 5·5 grams of lead acetate, and about 3 grams of caustic potash are required per gram of thiocarbamide.

Cyanamide is much more stable in the presence of alkalis, and in solution generally, than is commonly supposed. On the other hand, the dry substance has a tendency to explode spontaneously. C. F. B.

Mercuric Chlorothiocyanate. By CHARLES H. HERTY and J. G. SMITH (*J. Amer. Chem. Soc.*, 1896, **18**, 906—908).—The authors have investigated the compound described by McMurtry as mercuric chlorothiocyanate (Trans., 1889, 50), and have come to the conclusion that it is a definite chemical compound, and not merely a mixture of mercuric thiocyanate and mercuric chloride. J. J. S.

1:3-Dibromopropene [αγ-Dibromopropylene]. By ROBERT LESPIEAU (*Compt. rend.*, 1896, **123**, 1072—1073). — When a mixture of α-propenyl dibromhydrin and phosphoric anhydride is distilled, hydrogen bromide, tribromhydrin and β-epidibromhydrin, $CHBr\colon CH\cdot CH_2Br$, are obtained. The latter is a colourless liquid boiling at 155—156° and of sp. gr. = 2·097 at 0°; it solidifies when cooled to $-75°$, and melts again at $-52°$. It is not formed in the action of caustic potash on propenyl tribromhydrin. It can be converted into an acetin boiling at 175—177°, from which *bromallylic alcohol*, $CHBr\colon CH\cdot CH_2\cdot OH$, boiling at 169—170°, and of sp. gr. = 1·59 at 0°, can be obtained.

Methylic bromallylic ether boils at 127°, and *ethylic bromallylic ether* at 145°. All these compounds unite readily with two atoms of bromine, but in the case of the methylic ether substitution also occurs, and a new bromacrylic acid, $CHBr\colon CH\cdot COOH$, is formed, melting and decomposing at 140° (the two known isomerides melt at 115° and 70° respectively). Caustic potash removes 1 mol. HBr from these substances, giving rise to the corresponding acetylene compounds.

When β-epidibromhydrin is vigorously shaken with an aqueous solution of potassium cyanide, *bromocrotononitrile*, $CHBr\colon CH\cdot CH_2\cdot CN$, is formed, boiling at 95—98° (23 mm.), and from this *γ-bromocrotonic acid*, $CHBr\colon CH\cdot CH_2\cdot COOH$, melting at 58—59°, can be obtained. A. C. C.

Polymerisation of Olefine Hydrocarbons, I and II. By IWAN L. KONDAKOFF (*J. pr. Chem.*, 1896, [2], **54**, 442—454; 454—468).—Some zinc chloride was placed in a sealed tube, tertiary butylic chloride (1 mol.) added, the tube cooled to $-18°$, and isobutylene (1 mol.) passed in; the tube was then sealed, and allowed to remain at the ordinary temperature. The tertiary butylic chloride was obtained by allowing hydrochloric acid, saturated at 0°, to act on isobutylene in a sealed tube;

the isobutylene being prepared from isobutylic iodide and alcoholic potash. The zinc was used in amount equal to 10 per cent. of the hydrocarbon; if a larger quantity is used, the reaction is more rapid and energetic, but much larger quantities of tributylene, and even some tetrabutylene, are formed. After unchanged isobutylene and tertiary butylic chloride had been distilled off on the water-bath from the product of the reaction, and the residue had been freed from zinc by treatment with dilute acid, it was found best to treat it with moist silver oxide; an isodibutylene (octylene), and a little isotributylene then remained undissolved, whilst isodibutyl and tertiary butylic alcohol dissolved in the water, these resulting respectively from the action of the silver oxide on octylic chloride and on the residuary tertiary butylic chloride. The octylene boils at 101°—101·7°, and has a sp. gr. = 0·7326 at 0°/0°, and 0·7158 at 21°/21°; the isomeric substance obtained by Butleroff by the action of sulphuric acid on tertiary butylic alcohol boils at a temperature 1° higher, and has a sp. gr. = 0·7360 at 0°, but both substances yield the same derivatives when heated in a sealed tube at 100° with halogen acids saturated at −20°; the *octylic* (isodibutylic) *chloride* thus obtained boils at 40° under 13 mm. pressure, and has a sp. gr. = 0·8891 at 0°/0°, and 0·8756 at 18°/18°; the *bromide* boils at 62° under 18 mm. pressure and has a sp. gr. = 1·0634 at 0°/0°, and 1·0471 at 18°/18°; the *iodide* boils at 108—109° under 15 mm. pressure, and has a sp. gr. = 1·1122 at 0°/0°, and 1·0955 at 17°/17°. Probably both substances are mixtures of the two octylenes, the formation of which might be expected, namely $CH_2\colon CMe\cdot CH_2\cdot CMe_3$ and $CMe_2\colon CH\cdot CMe_3$, the first of these forming the chief constituent of Butleroff's substance, the second of the author's product. In the reaction studied by the author, the zinc chloride probably first forms a compound with the isobutylene; this then reacts with the tertiary butylic chloride, forming an octylic chloride, from which isobutylene withdraws hydrogen and chlorine, octylene and tertiary butylic chloride being produced.

"Trimethylethylene" and tertiary amylic chloride were allowed to react in the presence of zinc chloride, in the manner described above, except that the mixture was placed in flasks, instead of in sealed tubes. The tertiary amylic chloride was obtained by the action of hydrochloric acid, saturated at 0°, on "trimethylethylene." The latter was prepared by three different methods: by treating tertiary amylic alcohol with dilute sulphuric acid, or with oxalic acid, or by decomposing tertiary amylic iodide with alcoholic potash. The reaction takes place in the same way as with the butyl compounds. A diamylene (decylene), $C_{10}H_{20}$, was obtained; this boils at 154—159°, and has a sp. gr. = 0·7836 at 0°. It is apparently identical with the substance obtained by Erlenmeyer and by Wischnegradsky by acting on fermentation amylic alcohol with sulphuric acid; this substance boils at 154—159°, and has a sp. gr. = 0·7833 at 0°. When treated with halogen acids, both substances yield the same *decylic chloride*, boiling at 87—89° under 19 mm. pressure, and of sp. gr. 0·9011 at 0°/0° and 0·8894 at 14·5°/14·5°; *bromide*, boiling at 99—101° under 18 mm. pressure, and of sp. gr. 1·0420 at 0°/0° and 1·0071 at 18°/18°; and *iodide*, boiling at 114—116° under 16 mm. pressure, and of sp. gr. 1·2490 at 0°/0°, and 1·2340 at 14·5°/14·5°. All these compounds regenerate the original decylene when they are treated with alcoholic potash. Further, when the iodide is treated with moist silver oxide, *diamylene hydrate*, $C_{10}H_{21}\cdot OH$, is formed; this boils at 191—192°, and has a sp. gr. = 0·8380 at 0°/0°; it has the properties of an alcohol, and with phenylcarbimide yields a *phenylcarbamate*, which sublimes at 214° without melting, and crystallises from a mixture of alcohol and ethylic acetate in two forms, needles and short prisms. This points to the possibility of the decylene being really a mixture, which is all the more likely, as "trimethylethylene," which served as the starting-point, is known to contain unsymmetrical methylethylethylene. Very probably, the decylene consisted of $CMe_2\colon CMe\cdot CMe_2Et$, formed from trimethylethylene, and $CMe_2Et\cdot CH\colon CMeEt$, formed from methylethylethylene. A certain confirmation of this view was obtained, for methylethylcarbincarbinol, separated by Le Bel's method from the isobutylcarbinol that occurs mixed with it in fermentation amylic alcohol, was converted into the iodide, and then into methylethylethylene. This methylethylethylene boiled at 31—32°, and, with tertiary amylic chloride and zinc chloride, yielded a decylene which boiled at 157—157·5° under 759 mm. pressure, and had a sp. gr. = 0·7878 at 0°/0° and 0·7729 at 21°/21°. C. F. B.

Invert-Sugar, I and II. By JOHN HERON (*J. Fed. Inst. Brewing*, 1896, **2**, 440—452; 457—482). See this vol., ii, 194.

Preparation of Fatty Amines. By AUGUSTE TRILLAT (*Bull. Soc. Chim.*, 1896, [3], **15**, 321—322).—The author takes exception to Brochet's reply to his criticism of the conclusions drawn by Brochet and Cambier from their work on this subject. (Compare Abstr., 1896, i, 407.)

M. W. T.

Action of Methylic Alcohol on Magnesium Nitride. By EMERICH SZARVASY (*Ber.*, 1897, **30**, 305—309).—Methylic alcohol reacts energetically with magnesium nitride, and whether the two are heated at 270° in a sealed tube, or no extraneous heat is applied, large quantities of ammonia, trimethylamine, and hydrogen are produced, together with a solid residue of indefinite constitution.

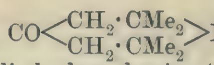
If, however, the compounds are allowed to react in a flask, fitted with a reflux condenser, and cooled in a freezing mixture, the evolved gases can be collected, and the proportions in which they are produced determined; this is found to be 40 per cent. of trimethylamine and 60 of ammonia.

The residue in the flask is a white, porous substance closely resembling magnesium oxide, which, from its analyses and reactions, is evidently *magnesium hydroxide methoxide*, $Mg(OH)\cdot OMe$, the action of the nitride on the alcohol being represented by the equation

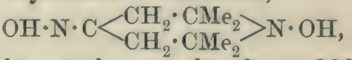
$$Mg_3N_2 + 6MeOH = 3Mg(OH)\cdot OMe + NH_3 + NMe_3.$$

Magnesium hydroxide methoxide is decomposed by water at the ordinary temperature, with production of magnesium hydroxide and methylic alcohol, whilst when dissolved in acids the corresponding magnesium salt and methylic alcohol are obtained. J. F. T.

Action of Hydroxylamine on Phorone. By CARL D. HARRIES and FRITZ LEHMANN (*Ber.*, 1897, **30**, 230—234).—The authors have submitted phorone to the action of hydroxylamine, and failed to obtain the normal oxime described by Naegeli (Abstr., 1883, 728); according to the experimental conditions, however, they have obtained three new substances.



Triacetonehydroxylamine, $\mathrm{CO}{<}\substack{\mathrm{CH_2\cdot CMe_2}\\ \mathrm{CH_2\cdot CMe_2}}{>}\mathrm{NOH}$, is prepared by heating phorone with alcoholic hydroxylamine (1 mol.) for 24 hours on the water bath; it crystallises from light petroleum, and melts at 50—51°. It dissolves readily in concentrated acids, and is precipitated from the solutions by alkalis; a cold, ammoniacal silver solution is reduced by the substance, and Fehling's solution when heated with it. The *hydrochloride* is crystalline. The *oxime*,



$$\mathrm{OH\cdot N\cdot C}{<}\substack{\mathrm{CH_2\cdot CMe_2}\\ \mathrm{CH_2\cdot CMe_2}}{>}\mathrm{N\cdot OH},$$

crystallises from light petroleum, and melts at 126—127°; it reduces Fehling's solution when heated.

The *base*, $C_9H_{18}N_2O_2$, is obtained by heating phorone with two molecular proportions of hydroxylamine, and when crystallised from light petroleum melts at 101—102°; it does not form an oxime, and is indifferent towards boiling Fehling's solution. The *hydrochloride* crystallises in small needles, and melts and decomposes at 165°; the *diacetyl* derivative crystallises from light petroleum in leaflets, and melts at 141°.

The action of hydroxylamine on mesitylic oxide has also been investigated.
M. O. F.

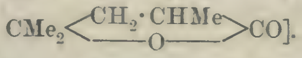
Synthesis of β-Hydroxy Acids. By SERGIUS N. REFORMATSKY (*J. pr. Chem.*, 1896, [2], **54**, 469—477).—This paper is a summary of results obtained by the author and his students, and already published in detail in the *J. Russ. Chem. Soc.* and in the *Berichte.* Evidence is now available to show that the action of zinc on a mixture of a halogen fatty acid, $CR^1R^2X\cdot COOR^3$ [R^1, R^2, R^3 = alkyl radicles or hydrogen, X = Cl, Br, or I], with a ketone, aldehyde, or formate, CR^4R^5O, [in this case R^5 may = OEt when R^4 = H; the R's may also be aromatic radicles] results in the successive formation of the following compounds, as representatives of all of these compounds have been isolated:—(1) $X\cdot Zn\cdot CR^1R^2\cdot COOR^3$; (2) $X\cdot Zn\cdot O\cdot CR^4R^5\cdot CR^1R^2\cdot COOR^3$; (3) $OH\cdot CR^4R^5\cdot CR^1R^2\cdot COOR^3$.

In the case of ethylic formate, the third stage is different, the compound (2) $X\cdot Zn\cdot O\cdot CH(OEt)\cdot CR^1R^2\cdot COOR^3$ yielding
(3) $X\cdot Zn\cdot O\cdot CH(CR^1R^2\cdot COOR^3)_2$, and this (4) $OH\cdot CH(CR^1R^2\cdot COOR^3)_2$.

In carrying out the reaction, the mixture of the ethylic salt of the halogen acid with the carbonyl compound was poured on to dry zinc, and allowed to remain until the odour of these substances had disappeared; water and dilute sulphuric acid were then added. The duration of the action varied from a few hours to several months, the yield being from 25 to 95 per cent. Ethylic chloracetate gave the best yields with ketones, but would not react with aldehydes. The other ethereal salts reacted readily with aldehydes, especially benzaldehyde, but only with difficulty with ketones, acetone excepted. The rule observed by Bischoff, that compounds containing many methyl groups in proximity are only formed with difficulty, was not confirmed by these researches, which lead but to the conclusion that "no definite generalisation can yet be made regarding the dynamic influence which the different groups exercise on the course of the reaction." C. F. B.

The Decomposition of β-Monhydroxy-acids. By SERGIUS N. REFORMATSKY (*J. pr. Chem.*, 1896, [2], 477—481).—A study has been made of the decomposition that 19 β-hydroxy-acids undergo, under the influence of sulphuric acid, of hydriodic acid, and when heated alone. The following are the generalisations made.

"As a rule, they lose water and form unsaturated acids, the water being formed from the hydroxyl group, and a hydrogen atom in the α- or γ-position, it is immaterial which; in the latter case, the βγ-unsaturated acid formed undergoes a further transformation into the lactone [$CHMe_2\cdot CH(OH)\cdot CHMe\cdot COOH \rightarrow CHMe_2\cdot CH{:}CMe\cdot COOH$, and $CMe_2{:}CH\cdot CHMe\cdot COOH$, or rather the corresponding lactone,



$$CMe_2<\begin{matrix}CH_2\cdot CHMe\\ O\end{matrix}>CO].$$

"If there is no hydrogen atom, either in the α- or in the γ-position, the aliphatic hydroxy-acids decompose into an aldehyde and an unsaturated acid ($OH\cdot CHMe\cdot CEt_2\cdot COOH \rightarrow CHMeO + CHEt_2\cdot COOH$); the aromatic ones yield a hydrocarbon, ($OH\cdot CHPh\cdot CMe_2\cdot COOH \rightarrow CHPh{:}CMe_2$); and the tertiary ones an alcohol and a hydrocarbon, ($OH\cdot CMe_2\cdot CMe_2\cdot COOH \rightarrow OH\cdot CMe_2\cdot CHMe_2$ and $CMe_2{:}CMe_2$).

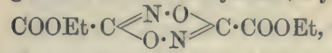
"Of the secondary hydroxy-acids containing the group CH in the α-position, the only ones that do not yield an unsaturated acid are those which contain the group $OH\cdot CHPh$; these, under the influence of sulphuric acid, decompose into carbonic anhydride and a hydrocarbon of the series C_nH_{2n-8}.

($OH\cdot CHPh\cdot CHMe\cdot COOH \rightarrow CO_2 + H_2O + CPh{:}CHMe$)."

C. F. B.

Stereoisomerism of Ethylic Isonitrosoacetoacetate. By MILORAD Z. JOVITSCHITSCH. (*Bull. Soc. Chim.*, 1896, [4], 15, 221—227).—The author has already pointed out (Abstr., 1896, 81, 82) the existence of two stereoisomeric forms of the compound $COMe\cdot C(N\cdot OH)\cdot COOEt$. These compounds could only be distinguished by the manner in which they behave when treated with potash, but he now brings forward further facts with regard to the relationship between them (Abstr., 1896, i, 81). When treated with 1 molecule of bromine, the bromine seems to displace an atom of hydrogen in the methyl group in the case of the *anti*-derivative, and, in the oximido-group, in the case of the *syn*-derivative. A second molecule of bromine displaces a hydrogen atom in the oximido-group of the *anti*-derivative, and in the methyl group of the *syn*-derivative. The substitution of bromine for hydrogen in the oximido-group is accompanied by a violent action.

The paper concludes with a note on the preparation of the isomeric ethylic isonitrosoacetoacetates. M. W. T.

Action of Fuming Nitric Acid on Ethylic Acetoacetate. By WALTER BECKH (*Ber.*, 1897, **30**, 152—156).—*Ethylic ββ-Dioximidosuccinate* which is best prepared by the etherification of Söderbaum's ββ-dioximidosuccinic acid, using the silver salt, is a crystalline compound, separating from ether, on the addition of light petroleum, as a fine powder, melting at 162°. On oxidation with gaseous nitrous anhydride, it yields *ethylic glyoximeperoxidedicarboxylate*,  $\mathrm{COOEt{\cdot}C}{<}\substack{\mathrm{N\cdot O}\\ \mathrm{O\cdot N}}{>}\mathrm{C{\cdot}COOEt}$, which is in every respect identical with the compound $C_8H_{10}N_2O_6$, obtained by Pröpper by the action of fuming nitric acid on ethylic acetoacetate. Pröpper did not obtain a sharp boiling point for this compound, but the author finds that it boils constantly at 159° under a pressure of less than 10 mm., whereas if the pressure is greater than this, no fraction of constant boiling point can be obtained. J. F. T.

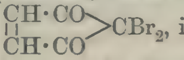
Moniodosuccinic Acid. By HEINRICH BRUNNER and ERNEST CHUARD (*Ber.*, 1897, **30**, 200—201. Compare Abstr., 1886, 576).—The salts of the moniodosuccinic acid, which is prepared by heating monobromosuccinic acid with alcoholic potassium iodide, are identical with those of the acid previously obtained by the authors by the action of iodine on the juices of certain fruits and plants. The free acid could not be obtained, since it decomposes, with formation of fumaric acid, when its solutions are evaporated. A. H.

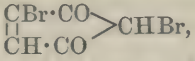
Action of Phenylcarbimide on γ-Pimelic Acid derived from Menthol. By GEORGES ARTH (*Bull. Soc. Chim.*, 1896, [4], **15**, 227—229).—Mehrländer has attempted to prove that the acid, $C_7H_{12}O_4$, which is obtained among the oxidation products of menthol, is identical with propylsuccinic acid. The author has shown that this is probably not the case, as the acid derived from menthol does not form an anhydride.

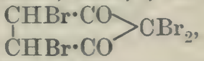
To confirm this view, he treated the latter acid with phenylcarbimide, and obtained its dianilide, but as this product did not give a phenylimide, $C_5H_{10}{:}(CO)_2{:}NPh$, on heating, he concludes that the original acid is incapable of forming an anhydride. (Compare Haller, Abstr., 1892, 1204). M. W. T.

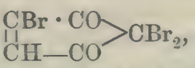
Normal Dilevulinic Acid (4 : 7-Decandiondioic Acid). By EDUARD A. KEHRER and ERWIN HOFACKER (*Annalen*, 1896, **294**, 165—182. Compare Abstr., 1895, i, 334).—*Normal dilevulinic (4 : 7-decandiondioic) acid*, $C_2H_4(CO{\cdot}CH_2{\cdot}CH_2{\cdot}COOH)_2$, is produced on heating δ-furfurylidenelevulinic acid with alcohol and concentrated hydrochloric acid for 2—3 hours in a reflux apparatus; it crystallises from water in lustrous, snow-white leaflets, and melts at 156—157°. The *ammonium* salt is crystalline, the *calcium* salt forms needles containing $2H_2O$, and the *hydrogen calcium* salt is anhydrous; the *barium* salt is microcrystalline, and contains $1H_2O$, and the methylic salt crystallises from water and melts at 98° (compare *loc. cit.*). The *phenylhydrazone* melts at 111—112°, and the *oxime* crystallises in colourless prisms and melts at 164—165°; the *silver* derivative of the oxime is amorphous. The *phenylhydrazone* and *oxime* of the methylic salt melt at 105° and 108—109° respectively; the *phenylhydrazone* and *oxime* of the ethylic salt melt at 104—105° and 129—130° respectively.

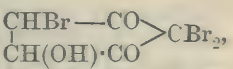
When normal dilevulinic acid is oxidised with nitric acid of sp. gr. = 1·3, the main product is succinic acid—small quantities of oxalic acid and hydrogen cyanide, along with a trace of formic acid, being also produced. M. O. F.

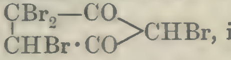
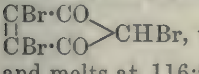
Derivatives of Pentamethylene and R-Pentene. By LUDWIG WOLFF and FRITZ RÜDEL (*Annalen*, 1896, **294**, 183—205).—2 : 2-*Dibromo*-1 : 3-*diketo*-R-*pentene*,  $\left.\begin{matrix}\mathrm{CH\cdot CO}\\ \mathrm{CH\cdot CO}\end{matrix}\right>\mathrm{CBr_2}$, is obtained by heating dibromolevulinic acid with 6 parts of a mixture of fuming sulphuric (1 part) and Nordhausen (3 parts) acids for 20 minutes at the temperature of boiling water; it crystallises from alcohol in rectangular plates, and melts at 137°.

2 : 4-*Dibromo*-1 : 3-*diketo*-R-*pentene*,  $\left.\begin{matrix}\mathrm{CBr\cdot CO}\\ \mathrm{CH\cdot CO}\end{matrix}\right>\mathrm{CHBr}$, is produced when the dibromo-acid is heated with 4 parts of a mixture of concentrated sulphuric and Nordhausen acids in equal proportions, and crystallises in white needles melting at 98·5—99°; the *azine* is obtained by treating the substance with an alcoholic solution of orthophenylenediamine, and crystallises from benzene in red needles melting at about 180°. Dichlorolevulinic acid yields the dichlorodiketopentene (m. p. 89°) described by Zincke and Fuchs (Abstr., 1893, i, 319).

2 : 2 : 4 : 5-*Tetrabromodiketopentamethylene*,  $\left.\begin{matrix}\mathrm{CHBr\cdot CO}\\ \mathrm{CHBr\cdot CO}\end{matrix}\right>\mathrm{CBr_2}$, is obtained by the action of bromine on 2 : 2-dibromodiketopentene dissolved in carbon bisulphide, and crystallises from petroleum in needles melting at 83°.

2 : 2 : 4-*Tribromodiketo*-R-*pentene*,  $\left.\begin{matrix}\mathrm{CBr\cdot CO}\\ \mathrm{CH{-}CO}\end{matrix}\right>\mathrm{CBr_2}$, arises from the tetrabromo-derivative under the influence of alcoholic sodium acetate (2 mols.); it crystallises from hot alcohol in lustrous leaflets, and melts at 120°.

2 : 2 : 4-*Tribromo*-5-*hydroxydiketopentamethylene*,  $\left.\begin{matrix}\mathrm{CHBr{-}CO}\\ \mathrm{CH(OH)\cdot CO}\end{matrix}\right>\mathrm{CBr_2}$, is produced when the tetrabromo-derivative is heated with 90 per cent. acetic acid; it crystallises in lustrous prisms, and melts at 146°.

2 : 4 : 4 : 5-*Tetrabromodiketopentamethylene*,  $\left.\begin{matrix}\mathrm{CBr_2{-}CO}\\ \mathrm{CHBr\cdot CO}\end{matrix}\right>\mathrm{CHBr}$, is obtained from the 2 : 4-dibromodiketopentene by the action of bromine, and crystallises from petroleum in long needles melting at 87°; alcoholic sodium acetate converts it into 2 : 4 : 5-*tribromodiketo*-R-*pentene*,  $\left.\begin{matrix}\mathrm{CBr\cdot CO}\\ \mathrm{CBr\cdot CO}\end{matrix}\right>\mathrm{CHBr}$, which crystallises from alcohol in prismatic needles and melts at 116·5°. When the tetrabromo-derivative is heated with methylic alcohol, a *methoxy*-compound is produced, and separates from petroleum in prismatic crystals melting at 126°.

Oxidation of 2 : 2-dibromodiketo-R-pentene with dilute nitric acid gives rise to dibromodinitromethane, along with fumaric and tribromacetylacrylic acids.

Tribromacetylacrylic acid, $\mathrm{CBr_3\cdot CO\cdot CH{:}CH\cdot COOH}$, crystallises from chloroform in small, white needles, sinters at 149°, and, when rapidly heated, melts at 156°; when heated with sodium carbonate, bromoform is eliminated, and maleic acid produced.

Tetrabromacetylacrylic acid, $CBr_3\cdot CO\cdot CBr\colon CH\cdot COOH$ or
$CBr_3\cdot CO\cdot CH\colon CBr\cdot COOH$,
is formed by the action of hypobromous acid on 2 : 2-dibromodiketo-R-pentene or by treating 2 : 2 : 4-tribromodiketo-R-pentene with dilute nitric acid ; it crystallises from hot water in prisms or needles, and melts at 160°.

Oxidation with 16 per cent. nitric acid converts 2 : 4-dibromodiketo-R-pentene into tribromonitromethane and bromofumaric acid.

βδ-dibromolevulinic anhydride is obtained by heating dibromolevulinic acid with acetic anhydride ; it crystallises from benzene in slender, white needles, and melts indefinitely at 138°. When heated with acetic anhydride for a long period of time, the substance yields an oily, neutral product, which gives rise to a small quantity of a crystalline substance when submitted to distillation ; this compound melts at 87°, and has the composition of a tribromodiketopentamethylene, $C_5H_3Br_3O_2$. M. O. F.

Derivatives of Butyltoluene. By ALBERT BAUR (THURGAU) (*Ber.*, 1897, **30**, 303—305).—When acetobutylorthotoluidide, melting at 164°, is nitrated, two products are formed. The *mononitro*-derivative melts at 147°, and is more soluble than the *dinitro*-derivative, which crystallises in needles and melts at 199°. The *mononitro*-base, obtained on hydrolysis, crystallises in brownish-red tablets, and melts at 81°, whilst the *dinitro*-base melts at 131°. The mononitro-base, on reduction, yields an amidobutyltoluidine, and this readily reacts with phenanthraquinone, forming a *phenazine*-derivative, which melts at 153°. The constitution of the mononitro-base is, therefore,

$$[Me : C_4H_9 : NO_2 : NH_2 = 1 : 3 : 5 : 6].$$

When it is diazotised, and the filtered solution boiled with alcohol, *mononitrobutyltoluene* $[Me : C_4H_4 : NO_2 = 1 : 3 : 5]$ is obtained as an oil which melts at 32° and boils at 120° (pressure = 15 mm.). Nitric acid converts it into a mixture of nitrocarboxylic acids. Mononitrobutyltoluene is accompanied by a *trinitrobutyltoluidine* which melts at 168°, and yields a *monethyl* derivative melting at 113°. Energetic nitration of the trinito-base yields an acid explosive substance which appears to have the formula $C_6(NO_2)_5\cdot NH\cdot NO$. A. H.

Benzoyldiazobenzene. By ARTHUR R. HANTZSCH and MARTIN SINGER (*Ber.*, 1897, **30**, 319—320).—In continuing their researches on the diazosulphones, the authors have had occasion to deal with E. Fischer's benzoyldiazobenzene, and although they have been unable to obtain any results bearing on the stereochemistry of the diazo-compounds, yet they have observed that it unites with gaseous hydrogen chloride, forming *benzoylorthochlorophenylhydrazine* ; this crystallises from boiling alcohol in white crystals melting at 152°.

The constitution of the compound follows from the fact that it yields benzoic acid and orthochlorophenylhydrazine on treatment with concentrated hydrochloric acid. J. F. T.

Conversion of Phenylhydrazine into Diazobenzene by Nitrous Acid. by JULIUS ALTSCHUL (*J. pr. Chem.*, 1896, [2], **54**, 496—508.)—

Nitrous acid, in the cold and in the presence of a strong mineral acid, oxidises phenylhydrazine to diazobenzene. For instance, 0·145 gram of pure phenylhydrazine hydrochloride was dissolved in 20 c.c. of water, the solution cooled, 2 c.c. of a di-normal sodium nitrite solution added, and then a mixture of 0·5 c.c. of strong hydrochloric acid with 2 c.c. of water; after an interval of 10 minutes or so, it was found that 80 per cent. of the phenylhydrazine had been converted into diazobenzene. This was ascertained by extracting the liquid twice with ether, to remove nitrosophenylhydrazine, and pouring it into an excess of a N/10 solution of sodium β-naphtholdisulphonate ("R-salt"), the excess of which was then titrated with a N/10 diazotoluene solution. The diazobenzene is formed by the direct action of the nitrous acid on the phenylhydrazine, and not by the decomposition, theoretically possible, of nitrosophenylhydrazine first formed into diazobenzene and hydroxylamine, for a solution of nitrosophenylhydrazine in cold hydrochloric acid gives no azo-dye when poured into the R-salt solution.

C. F. B.

Diazotisation of Aniline in the presence of Acetic Acid, or of an Insufficient Amount of Hydrochloric Acid. By Julius Altschul (*J. pr. Chem.*, 1896 [2], **54**, 508—510).—Aniline is diazotised to the extent of about 20 per cent. in the presence of 2½ mols. of acetic acid, completely in the presence of 11 mols.

Aniline hydrochloride is diazotised only partially by sodium nitrite if no excess of acid is added. The diazotisation increases with the concentration of the solution; in solutions containing, respectively, 10, 1, and 0·1 per cent. of aniline, about 30, 20, and 10 per cent. of the aniline was diazotised.

C. F. B.

Action of Bleaching Powder Solution on Phenylhydrazine. Formation of Azobenzene. By Heinrich Brunner and Louis Pelet (*Ber.*, 1897, **30**, 284—285).—When phenylhydrazine is treated with bleaching powder solution, azobenzene and benzene are formed; in the early stages of the reaction a smell of nitrobenzene is noticed.

A. H.

Comparative Experiments with Normal and Iso-diazotates. By Eugen Bamberger (*Ber.*, 1897, **30**, 211—219. Compare Abstr., 1896, i, 299).—As shown by von Pechmann (Abstr., 1894, i, 282), normal diazobenzene sodium and diazoparatoluene sodium, when acted on by acid chlorides, are converted into the nitroso-derivative of the corresponding acid anilide. The potassium salts behave in a similar manner, normal diazobenzene potassium and normal diazoparatoluene potassium being converted by benzoic chloride into nitrosobenzanilide and nitrosobenzotoluidide. The iso-salts, however, do not undergo this change, but are converted into the normal salts, a very small amount of the nitrosoanilide being sometimes formed from these by the action of the chloride or anhydride. It seems probable that the iso-salt first reacts in the sense of the equation,

$$\mathrm{PhN_2{\cdot}OK + ClCOPh = PhN_2Cl + Ph{\cdot}COOK},$$

and that the diazonium chloride thus produced is converted into the normal diazo-salt by the alkali present. This is confirmed by the fact that, when isodiazobenzene potassium and picric chloride are brought together in alcoholic solution, a considerable amount of potassium picrate is precipitated, whilst the filtrate reacts with β-naphthol solution to form phenylazo-β-naphthol.

Behaviour of normal and isodiazotates towards sodium amalgam [with N. Rongger]. When the potassium salts of isodiazobenzene and its substitution derivatives are treated with sodium amalgam, they yield no hydrazine, or only a small amount, whereas the salts of the normal compounds yield a large proportion of hydrazine. The following table gives the experimental results obtained, the numbers in the two columns expressing the percentage of the theoretical yield of hydrazine which was actually produced. The potassium salt of isoparasulphodiazobenzene yields much more hydrazine than any of the other isocompounds, but still less than the corresponding normal salt.

		Normal	Iso.
Diazobenzene potassium	(1)	0	72
	(2)	0	75
Parachlorodiazobenzene potassium ...	(1)	7	74
	(2)	0	
Parabromodiazobenzene potassium ...	(1)	0	54
	(2)	0	
Parasulphodiazobenzene potassium ...	(1)	28	63
	(2)	31	70

Parachlorophenylhydrazine melts at 88°, and not at 83° as usually stated. *Acetone-parachlorophenylhydrazone* forms silvery white, flat needles which have a satiny lustre, and melt at 84°. It is rapidly converted into a resinous mass on exposure to the air.

A. H.

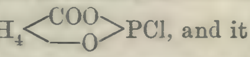
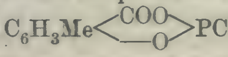
Diquinoyltrioxime and Tetranitrophenol. By Rudolf Nietzki and F. Blumenthal (*Ber.*, 1897, 30, 181—186).—*Diquinoyltrioxime*, $C_6H_2O(N\cdot OH)_3$, which is formed together with the tetroxime by the action of hydroxylamine hydrochloride on dinitrosoresorcinol, is distinguished from it by its insolubility in the usual indifferent solvents. It is purified by means of the *ammonium* salt, which crystallises in yellowish-red needles. The free oxime is a brownish-yellow, crystalline powder, which deflagrates at about 250° without melting; when treated in the cold with acetic anhydride, it is converted into a *diacetate* which melts at 142°, and cannot be recrystallised without undergoing decomposition. If this diacetate is heated with acetic anhydride, the *anhydride* of the oxime, $C_6H_3N_3O_3$, is formed; this crystallises in almost colourless, stellate groups of needles, melts at 181°, and gives an intense green coloration with ferrous salts. The *ferrous* salt, $(C_6H_4N_3O_4)_2Fe$, which is thus formed, can readily be isolated and recrystallised from ethylic acetate.

When the trioxime is treated with stannous chloride and hydrochloric acid, it is reduced to triamidophenol. The *sulphate* of this base, $C_6H_9N_3O,H_2SO_4$, is only very sparingly soluble in water; the *picrate* has also been prepared. Triamidophenol gives a blue coloration with ferric chloride; its *triacetyl* derivative melts at 230°, and the *tetracetyl* derivative at 211°.

It was found impossible to bring about a simple oxidation of the

trioxime. Dilute nitric acid, however, converts it into tetranitrophenol, $C_6H(NO_2)_4 \cdot OH$, which probably has the asymmetric constitution, $[OH : (NO_2)_4 = 1 : 2 : 3 : 4 : 6]$; this crystallises in broad, golden-yellow needles, with a violet iridescence, and melts at 130°, often with a somewhat violent explosion. It dyes wool and silk a redder shade than picric acid. Its salts are extremely explosive; the *sodium* salt crystallises in reddish-yellow needles, the *barium* salt in dark yellow prisms, whilst the *silver* salt forms a reddish-yellow, crystalline precipitate.
A. H.

A Law of Production of Phenolcarboxylic Chlorides. By RICHARD ANSCHÜTZ (*Ber.*, 1897, **30**, 221—223).—Study of the behaviour of hydroxybenzoic acids towards phosphorus pentachloride has led to the following generalisation. Orthohydroxybenzoic acids yield the free phenolcarboxylic chlorides on treatment with phosphorus pentachloride, when the second ortho-position with regard to the hydroxy-group is already occupied; if this is not the case, the phosphorus oxychloride derivative of the corresponding phenolcarboxylic chloride is produced. The following compounds have been prepared. 3-*Methyl-*, 3-*chloro-*, and 3-*nitrosalicylic chlorides*, melting at 27—28°, 62—63°, and 60° respectively; 3 : 5-*dichloro-*, 3 : 5-*dibromo-*, 3 : 5-*di-iodo-*, and 3 : 5-*dinitro-salicylic chlorides*, melting at 79°, 87°, 67—68°, and 69—70° respectively; 5 : 3-*chloronitrosalicylic chloride* is liquid, and 5 : 3-*bromonitro-*, and 3 : 5-*bromonitro-salicylic chlorides* melt at 56·5° and 51° respectively. *Hydroxyuvitic dichloride* melts at 67—68°, and *α-hydroxy-β-naphthoic chloride* at 82—84°; 3 : 5-*dichlorosalicylic anhydride* melts at 186—187°.

The author has previously shown that phosphorus trichloride converts salicylic acid into salicylochlorophosphine,  $C_6H_4\left<\begin{matrix}COO\\ O\end{matrix}\right>PCl$, and it is now found that a substituent in the ortho-position with regard to the hydroxy-group affords no protection to the latter; *orthomethylsalicylochlorophosphine*,  $C_6H_3Me\left<\begin{matrix}COO\\ O\end{matrix}\right>PCl$, is obtained by the action of phosphorus trichloride on orthomethylsalicylic acid, and melts at 36—37°.
M. O. F.

Action of Ethylic Cyanoacetate and of Benzylic Cyanide on Aldehydes, Ketones, and Aldehyde-Ammonia. By FR. RIEDEL (*J. pr. Chem.*, 1896, [2], **54**, 533—555. Compare Carrick, Abstr., 1892, 1086; Bechert, Abstr., 1894, i, 488; and Frost, Abstr., 1889, 597).—*Ethylic parahydroxy-α-cyanocinnamate*, $OH \cdot C_6H_4 \cdot CH \vdots C(CN) \cdot COOEt$, is readily obtained by the action of small quantities of sodium ethoxide on a solution of parahydroxybenzaldehyde and ethylic cyanoacetate in absolute alcohol. It separates from its alcoholic solution in yellow crystals, melts at 162—163°, and is readily soluble in all organic solvents, with the exception of light petroleum. On boiling with acetic anhydride, it is converted into its *acetyl* derivative, $OAc \cdot C_6H_4 \cdot CH \vdots C(CN) \cdot COOEt$, which crystallises in colourless, glistening plates, and melts at 87·5°. A chloroform solution of bromine readily reacts with ethylic parahydroxy-α-cyanocinnamate, even in the cold, to form a *compound*, $C_{19}H_{16}N_2BrO_3$, which melts at 183°. The action of bromine in the cold on the acetyl derivative is also complex, hydrogen bromide being evolved. Sodium ethoxide hydrolyses the ethylic salt to *sodium-a-paradihydroxybenzylmalonate*, which, on treatment with hydrochloric acid, yields the *free acid*, $OH\cdot C_6H_4\cdot CH(OH)\cdot CH(COOH)_2$, melting at 232°.

Ethylic orthonitro-a-cyanocinnamate, $NO_2\cdot C_6H_4\cdot CH{:}C(CN)\cdot COOEt$, crystallises from absolute alcohol in glistening plates, melts at 96°, and is readily soluble in most organic solvents with the exception of light petroleum. It is not acted on by bromine in the cold. The ethylic salt can best be hydrolysed by dissolving it in alcohol, precipitating by hot water and adding sodium hydroxide in small portions at a time; before the addition of fresh soda, it is necessary to wait until the alkaline reaction disappears, and also to keep the temperature below 70°. The *acid* thus obtained melts at 223°.

Ethylic metanitro-a-cyanocinnamate melts at 127—128°, and the corresponding acid at 172°.

Methylenediphenylacetamide, $CH_2(NH\cdot CO\cdot CH_2Ph)_2$, is readily obtained when hydrogen chloride is passed through a mixture of benzylic cyanide and methylal. The same compound has already been obtained by Hepp (Abstr., 1878, 66).

Benzylic cyanide and deoxybenzoin act on one another in the presence of a small quantity of sodium ethoxide dissolved in alcohol, forming the compound $CN\cdot CPh{:}CPh\cdot CH_2Ph$ [*αβγ-triphenylcrotonitrile*], which, after recrystallisation from a mixture of alcohol and acetic acid, melts at 212°.

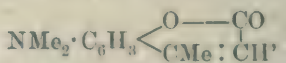
Ethylic cyanoacetate also reacts with deoxybenzoin under similar conditions, with formation of a compound, $COOEt\cdot C(CN){:}CPh\cdot CH_2Ph$ [*ethylic a-cyano-βγ-diphenylcrotonate*], which melts at 163°.

Although ethylic cyanoacetate does not form condensation products with acetaldehyde itself, it reacts with aldehyde-ammonia either alone or, still better, in alcoholic solution. The product, $C_7H_{10}N_2O_2$, is insoluble in all organic solvents, and is best recrystallised from boiling water; on prolonged boiling, however, with water, paraldehyde is formed. The compound has no definite melting point, as it decomposes on heating. Dilute alkalis and acids decompose it, yielding ammonia; alcoholic ammonia also reacts with the substance under pressure, yielding a compound $C_6H_9N_2O$.

Diacetonitrile also reacts with aldehyde-ammonia, yielding small quantities of a compound $C_4H_9N_2O$ (?), the constitution of which could not be determined.

Cyanacetic and malonic acids, ethylic malonate, and ethylic acetoacetate, all react with aldehyde-ammonia; the products thus formed are white, crystalline compounds, which could not be closely investigated, on account of the readiness with which they decompose. J. J. S.

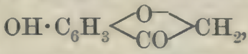
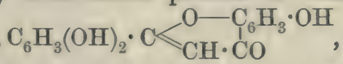
Basic Coumarins. By Hans von Pechmann (*Ber.*, 1897, 30, 277—278).—The synthesis of coumarins from ethylic acetoacetate and phenols is applicable to amidophenols, which give rise to amidocoumarins and their derivatives.



Dimethylamido-β-methylcoumarin, $NMe_2\cdot C_6H_3{<}\begin{array}{l}O{-}{-}CO\\ CMe{:}CH\end{array}$, obtained from ethylic acetoacetate and dimethylmetamidophenol, crystallises from alcohol in yellowish needles, exhibiting greenish fluorescence; it melts at 143°, and effloresces in dry air, becoming colourless.

The solutions in alcohol and ether exhibit violet fluorescence, and the salts of mineral acids have a copper-red fluorescence.

M. O. F.

Flavone Derivatives, IV. By J. BRÜLL and PAUL FRIEDLAENDER (*Ber.*, 1897, **30**, 297—302. Compare Abstr., 1896, i, 607).—Diacetylresacetophenone is best prepared by heating resacetophenone with acetic anhydride and sodium acetate for a short time, and pouring the mass into water. On bromination, it yields derivatives containing bromine in the nucleus, as well as an oily product containing bromine in the side chain; the latter is converted by alkalis into metahydroxyketocoumaran,  $OH\cdot C_6H_3<\begin{matrix}O\\CO\end{matrix}>CH_2$, which has previously been described. The *acetate* crystallises in long needles, and melts at 80·5°. Hydroxyketocoumaran readily reacts with aldehydes, yielding products identical with those obtained by the action of aldehydes on the oily bromination product of diacetylresacetophenone. *Trihydroxyflavone*,  $C_6H_3(OH)_2\cdot C<\begin{matrix}O—C_6H_3\cdot OH\\ \quad\;\; | \\ CH\cdot CO\end{matrix}$, is obtained by condensation with protocatechuic aldehyde, and crystallises in slender, bright yellow needles. The alkaline solution is reddish-violet, whilst the solution in sulphuric acid is orange red. The *triacetate*, which crystallises in colourless needles melting at 168°, dyes orange-yellow shades on alumina, and brown on iron or chromium mordants. The *dihydroxyflavone* obtained from metahydroxybenzaldehyde crystallises in yellow needles decomposing at about 240°, and forms yellow solutions in sulphuric acid and in aqueous soda. Acetylpeonol, on bromination, yields a *monobromopeonol*, $OMe\cdot C_6H_2Br(OH)\cdot CO\cdot CH_3$, which crystallises in long, white needles melting at 171°. It is accompanied by the monobromacetylpeonol, $OMe\cdot C_6H_3(OAc)\cdot CO\cdot CH_2Br$, which has been previously described. The further action of bromine on monobromopeonol yields a mixture of derivatives which has not been carefully examined.

Monobromacetylpeonol reacts with benzaldehyde to form *metamethoxyflavone*, $C_{16}H_{12}O_3$, which crystallises in plates, and melts at 143·5°. It was found impossible to prepare a methoxyketocoumaran by the action of alkalis on the bromide. The *compound* with piperonal forms lustrous, yellow plates melting at 175°, and gives an eosin-red coloration with sulphuric acid. The *compound* with furfuraldehyde crystallises in yellowish needles melting at 136°.

A. H.

A Dye derived from Dibromogallic Acid. By ALEXANDRE BIÉTRIX (*Bull. Soc. Chim.*, 1896, [4], **15**, 235—236).—The author has examined the brown substance formed by the oxidation of an alkaline solution of dibromogallic acid when it is exposed to the air. He finds that a bromide and carbonate are formed, and at the same time a salt of an organic acid, which is precipitated on adding hydrochloric acid. The acid is insoluble in all organic solvents, is violently attacked by nitric acid with formation of oxalic acid, but does not react with acetic chloride or acetic anhydride. The barium salt has, from analysis, the composition $C_{12}H_8Ba$.

The dye is of little use from a practical point of view. M. W. T.

Dinitrodiphenylethylenedisulphone. By HEINRICH LIMPRICHT [and PAROW] (*Annalen*, 1896, **294**, 243—252. Compare Abstr., 1894, i, 292).—*Dinitrodiphenylethylenedisulphone*, $C_2H_4(SO_2\cdot C_6H_4\cdot NO_2)_2$, is obtained by the action of ethylenic bromide (1 mol.) on sodium metanitrobenzenesulphinate (compare *loc. cit.*); it crystallises in white needles, melts at 226°, and is scarcely soluble in boiling organic solvents. *Diamidodiphenylethylenedisulphone*, $C_2H_4(SO_2\cdot C_6H_4\cdot NH_2)_2$, dissolves sparingly in boiling alcohol, and melts at 245°; the *hydrochloride* blackens at 275°, and effervesces at 295°. The *sulphate* crystallises in slender needles, and on adding sodium nitrite to the solution, and then treating it with copper powder, a *compound* is obtained which melts at 266°, and probably has the constitution $C_2H_4(SO_2\cdot C_6H_4\cdot OH)_2$.

Nitrophenylsulphone-ethylic alcohol, $NO_2\cdot C_6H_4\cdot SO_2\cdot CH_2\cdot CH_2\cdot OH$, is prepared by treating ethylenedinitrophenyldisulphone with boiling, aqueous alkali (1 mol.), and crystallises from ether in large, colourless prisms melting at 78·5°; the *methylic* and *ethylic* ethers melt at 72° and 93° respectively. If excess of alkali is employed in preparing this substance, a *compound* is formed which crystallises from alcohol in yellow needles and melts at 133°; it probably has the constitution $O(C_2H_4\cdot SO_2\cdot C_6H_4\cdot NO_2)_2$.

Amidophenylsulphone-ethylic alcohol, $NH_2\cdot C_6H_4\cdot SO_2\cdot CH_2\cdot CH_2\cdot OH$, is obtained by the action of alkali on diamidodiphenylethylenedisulphone, and by reducing nitrophenylsulphone-ethylic alcohol; the *hydrochloride* crystallises in prisms, and melts at 210°, and the *platinochloride* crystallises in small, yellow prisms.

Nitrophenylsulphone-acetic acid, $NO_2\cdot C_6H_4\cdot SO_2\cdot CH_2\cdot COOH$, is prepared by oxidising the alcohol with potassium permanganate or potassium dichromate, and crystallises from ether in white needles melting at 57°; the *potassium* and *silver* salts form white needles.

Dinitrodiphenyldisulphonediethylamine, $NH(C_2H_4\cdot SO_2\cdot C_6H_4\cdot NO_2)_2$, arises from dinitrodiphenylethylenedisulphone under the influence of moderately concentrated ammonia at 110°, and crystallises in slender needles melting at 125°; the *nitrate* forms leaflets and prisms, and melts at 205°, and the *hydrochloride* crystallises in slender, white needles, melting at 204°.

Diamidodiphenyldisulphonediethylamine, $NH(C_2H_4\cdot SO_2\cdot C_6H_4\cdot NH_2)_2$, is obtained from the foregoing compound on reduction with stannous chloride; the *hydrochloride* forms yellowish prisms, darkens at 230°, and melts at 235°. M. O. F.

Action of Diazo-compounds on Benzenesulphinic Acid. By ARTHUR R. HANTZSCH and MARTIN SINGER (*Ber.*, 1897, **30**, 312—319).—The authors have prepared a large number of diazosulphones by the action of diazo-compounds on benzenesulphinic acid, in the hope of obtaining further instances of stereoisomerism in the diazo-derivatives; the diazosulphones obtained, however, appear to be, without exception, *anti*-compounds, analogous to the *anti*-diazosulphonates, the corresponding *syn*-derivatives seeming incapable of existence.

Paratoluenediazophenylsulphone, $C_6H_4Me\cdot N_2\cdot SO_2Ph$, from diazoparatoluidine and benzenesulphinic acid, crystallises from alcohol in slender, yellow needles decomposing at 90°.

Orthoanisoildiazophenylsulphone, $OMe\cdot C_6H_4\cdot N_2\cdot SO_2Ph$, prepared from orthanisidine, crystallises from alcohol in golden needles melting at 104°, the corresponding *para*-derivative from paranisidine melts at 73—74°.

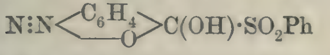
Parachlorobenzenediazophenylsulphone, $C_6H_4Cl\cdot N_2\cdot SO_2Ph$, from *para*-chlorodiazobenzene chloride, crystallises from boiling alcohol in yellow needles melting at 102—103°; this compound is also produced by the action of *syn*-chlorobenzenediazocyanide on benzenesulphinic acid, the *anti*-diazocyanide also producing the same compound.

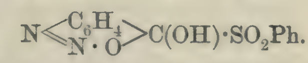
Parabromobenzenediazophenylsulphone forms yellowish-red needles melting at 116°. It is reduced by zinc dust in glacial acetic acid solution to parabromophenylsulphazide melting at 162°.

Tribromobenzenediazophenylsulphone $[Br_3 : N_2SO_2Ph = 2:4:6:1]$, from tribromodiazobenzenesulphate, decomposes at 122°.

a-Naphthalenediazophenylsulphone, $C_{10}H_7\cdot N_2\cdot SO_2Ph$, is obtained in golden plates melting at 95°; the corresponding β-derivative cannot be obtained in a pure state.

Paradiazobenzoic acid phenylsulphone, $COOH\cdot C_6H_4\cdot N_2\cdot SO_2Ph$, from the chloride of paradiazobenzoic acid, crystallises from hot alcohol in garnet-red needles, decomposing at 122—123°. The corresponding compound, produced by the condensation of orthodiazobenzoic acid with benzenesulphinic acid, is quite different; it crystallises from hot glacial acetic acid in white prisms melting at 169—170°, is insoluble in alkali carbonates, very stable towards ammonia and alkali hydroxides, and, lastly, it combines with β-naphthol. From these considerations, it seems probable that, whilst the para-compound is the true carboxylic acid of the diazosulphone, the compound derived from orthodiazobenzoic acid is either, I, an inner diazonium salt, or, II, an inner *syn*-diazoanhydride, formed by the benzenesulphinic acid attaching itself to the carbonyl group of the diazoanthranilic acid.

I. 
$N{:}N<\begin{smallmatrix}C_6H_4\\ O\end{smallmatrix}>C(OH)\cdot SO_2Ph$

II. 
$N<\begin{smallmatrix}C_6H_4\\ N\cdot O\end{smallmatrix}>C(OH)\cdot SO_2Ph.$

On heating the compound with water in a closed tube at 120—230°, salicylic acid is produced. J. F. T.

Orthotoluenesulphinic Acid. By Julius Troeger and Walther Voigtländer-Tetzner (*J. pr. Chem.*, 1896, [2], 54, 513—532).—Sodium orthotoluenesulphinate, $C_7H_7SO_2Na + 4H_2O$, is easily prepared from the product formed by the action of a mixture of zinc dust and water on orthotoluenesulphochloride by treating it with sodium carbonate. It is most conveniently purified by converting it into the free acid and again neutralising with sodium carbonate. It is difficult to obtain this salt in well-developed crystals, as it is so very soluble both in water and in 95 per cent. alcohol, although insoluble in absolute alcohol and ether. The *barium* salt, $(C_7H_7SO_2)_2Ba + 3H_2O$, and the *strontium* and *calcium* salts, which also crystallise with $3H_2O$, are described. The acid itself (compare Limpricht, Abstr., 1887, 723) is extremely soluble in water, and melts at 80°. On boiling with water for about 3 hours, the sulphinic acid is converted into *orthotoluic disulphoxide*, $(C_7H_7)_2S_2O_2$, which separates as an oil, and orthotoluenesulphonic acid, which remains in solution. The disulphoxide separates from its alcoholic solution in glistening crystals, and melts at 95—96°. It is insoluble in water, but readily soluble in alcohol or ether. A similar decomposition occurs when the sulphinic acid is neutralised with sodium carbonate unless care is taken to keep the mixture cool. The disulphoxide, on treatment with zinc dust, yields zinc toluenesulphinate and the zinc derivative of tolylic hydrosulphide; and on warming it with potash (1 : 2), it yields *orthotolylic bisulphide*, which crystallises from its alcoholic solution in yellowish plates melting at 38°; the byeproducts consist of orthothiocresol and potassium orthotoluenesulphinate. On reduction in the cold with zinc and hydrochloric acid, sodium orthotoluenesulphinate is converted into orthotolylic bisulphide and orthothiocresol; if, however, the mixture is not kept cool, the sulphonic acid and disulphoxide are obtained. If hydrogen sulphide is passed through a methyl alcoholic solution of the sulphinic acid for 40 hours, *orthotolylic pentasulphide*, $(C_7H_7)_2S_5$, and *orthotolylic tetrasulphide*, $(C_7H_7)_2S_4$, are formed. Both these compounds are oils, but whilst the pentasulphide separates during the reaction, the tetrasulphide remains dissolved in the alcohol. Chlorine converts sodium orthotoluenesulphinate into orthotoluenesulphochloride, and bromine into *orthotoluenesulphobromide* (m. p. 90°).

The following alkylsulphones, $C_7H_7SO_2R$, have been obtained by the action of alkylic iodides on sodium orthotoluenesulphinate: *Methyl-*, *ethyl-*, *normal* and *iso-propyl-*, *normal* and *iso-butyl-*; *normal amyl-*, *β-hexyl-*, and *benzyl-orthotolylsulphones*, all of which are oily substances. *Orthotolylcetylsulphone*, $C_7H_7\cdot SO_2\cdot C_{16}H_{33}$, crystallises in needles and melts at 65°. These monosulphones cannot be hydrolysed, and are not acted on by reducing agents.

Diorthotolylethylenedisulphone, $C_2H_4(SO_2\cdot C_7H_7)_2$, obtained by warming an alcoholic solution of the sodium sulphinate with ethylenic dibromide for 20 hours on the water bath, melts at 94—95°. It is not readily reduced, but can be hydrolysed by 33 per cent. potassium hydroxide solution, yielding *orthotolylsulphonethylic alcohol*, $C_7H_7\cdot SO_2\cdot CH_2\cdot CH_2\cdot OH$, and potassium orthotoluenesulphinate.

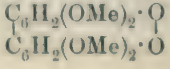
Diorthotolylpropylenedisulphone, $C_7H_7\cdot SO_2\cdot CHMe\cdot CH_2\cdot SO_2\cdot C_7H_7$, *diorthotolyltrimethylenedisulphone*, $C_7H_7\cdot SO_2\cdot (CH_2)_3\cdot SO_2\cdot C_7H_7$, *triorthotolylpropenyltrisulphone*, $C_3H_5(SO_2\cdot C_7H_7)_3$, and *orthotolylallylsulphone*, $C_3H_5\cdot SO_2\cdot C_7H_7$, are all oily substances; the compound last mentioned combines with bromine, forming an oily *dibromide*, whilst at 150°, with hydrogen bromide, it yields *orthotolylbromopropylsulphone*,

$$CH_3\cdot CHBr\cdot CH_2\cdot SO_2\cdot C_7H_7,$$

which is also an oil.

Orthotolylsulphonacetone, $C_7H_7\cdot SO_2\cdot CH_2\cdot COMe$, obtained by the action of monochloracetone on sodium orthotolylsulphinate, is an oil, and yields an oily *oxime* and *hydrazone*. J. J. S.

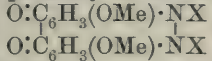
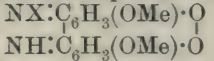
Cœrulignone Colouring Matters. By Carl T. Liebermann and Julian Flatau (*Ber.*, 1897, **30**, 234—242).—Cœrulignone,



$$\begin{array}{l} C_6H_2(OMe)_2\cdot O \\ | \qquad\qquad\qquad\;\; | \\ C_6H_2(OMe)_2\cdot O \end{array}$$

combines with primary aromatic bases, forming beautiful, blue colouring matters, in accordance with the equation,

$$C_{16}H_{16}O_6 + 2NH_2X = 2CH_3{\cdot}OH + C_{14}H_{12}O_4(NX)_2 ;$$

this change is generally applicable to aromatic primary amines which are not readily oxidised, but secondary and tertiary bases are indifferent towards cœrulignone. The colour bases produced in this manner probably have the constitution expressed by one of the formulæ,  $\begin{matrix} O{:}C_6H_3(OMe){\cdot}NX \\ | \qquad\qquad\quad | \\ O{:}C_6H_3(OMe){\cdot}NX \end{matrix}$ and  $\begin{matrix} NX{:}C_6H_3(OMe){\cdot}O \\ | \qquad\qquad\quad | \\ NH{:}C_6H_3(OMe){\cdot}O \end{matrix}$; they are easily reduced to leuco-compounds by treatment with sulphurous acid.

Dianilidodimethoxydiphenylquinone (*lignone-blue*), $C_{14}H_{12}O_4(NPh)_2$, is obtained on adding aniline to cœrulignone with hot acetic acid; it crystallises from chloroform in lustrous needles containing the solvent, which, however, is removed on heating at 110°, the crystals losing their lustre. *Paratoluidodimethoxydiphenylquinone* (*paradimethyl-lignone blue*), $C_{14}H_{12}O_4(N{\cdot}C_6H_4Me)_2$, crystallises from the blue, chloroform solution in needles having a metallic lustre; the spectrum of the solution exhibits two bands near the D line.

Hexamethyl-lignone-blue, *paradibromolignone-blue*, *metadichlorolignone-blue*, *orthodimethoxylignone-blue*, *lignone-blue-orthodicarboxylic acid*, and *lignone-blue-metadicarboxylic acid*, have been also prepared; *sodium lignone-blue-paradisulphonate* is obtained from cœrulignone, acetic acid, and sodium sulphanilate. M. O. F.

Reactions distinctive of the Rosanilines and of Carbinols containing Amido-groups. By AUGUSTE ROSENSTIEHL (*Bull. Soc. Chim.*, 1896, [3], **15**, 327—330).—The author criticises the work of Prud'homme on the constitution of 'patent blue' (Abstr., 1896, i, 735). This substance, although it had never been isolated, or analysed by Prud'homme, judging from its reactions, has the formula of a carbinol derivative. The formation of a benzidine derivative when it is oxidised by lead peroxide, and the permanency of the colour in the presence of alkalis, supposed by Prud'homme to be characteristic of a carbinol, are shown by the author to be equally characteristic of the rosanilines.

M. W. T.

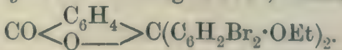
Quinoidal Derivatives of Phenolphthalein. By RUDOLF NIETZKI and EDUARD BURCKHARDT. (*Ber.*, 1897, **30**, 175—180).—Herzig's ethylic salt of phenolphthalin does not, like the corresponding fluorescein derivative, yield a quinoidal ethylic salt on oxidation; the tetrabromoderivative, however, does so readily.

The *ethylic* salt of *tetrabromophenolphthalin*, produced by the action of bromine on a solution of the ethylic salt of phenolphthalin in glacial acetic acid solution, crystallises from this solvent in colourless needles melting at 163°; on treatment with acetic anhydride, it yields a *diacetyl* derivative melting at 231°. When pure, its solution in alkali is colourless, but on oxidation with potassium ferricyanide, a blue precipitate is obtained, which is the potassium salt of the *quinoidal ethylic* salt of *tetrabromophenolphthalin*. The free *ethylic salt*,

$$O{:}C_6H_2Br_2{:}C(C_6H_2Br_2{\cdot}OH){\cdot}C_6H_4{\cdot}COOEt,$$

is best produced by dissolving the potassium salt in water, and covering the solution with benzene; on cautiously acidifying with acetic acid and shaking the mixture while in the water bath, the ethylic salt is dissolved by the benzene, and separates out on cooling in yellow needles containing benzene of crystallisation. The compound crystallises from alcohol in blood-red prisms melting at 210—215°, and is a powerful dye, colouring wool and silk a nearly pure blue. It is a remarkable instance in favour of the chemical theory of dyeing; for a carefully acidified solution of its alkali salt, although nearly colourless, dyes a piece of silk or wool immersed in it an intense blue.

By the double decomposition of the potassium salt with silver nitrate and the action of ethylic iodide on the silver salt thus obtained, the *diethylic salt*, $O{:}C_6H_2Br_2{:}C(C_6H_2Br_2{\cdot}OEt){\cdot}C_6H_4{\cdot}COOEt$, is produced; this crystallises from light petroleum in sulphur-yellow needles melting at 150—151°. On partial hydrolysis with dilute sulphuric acid, this salt yields the *monethylic* ether, $O{:}C_6H_2Br_2{:}C(C_6H_2Br_2{\cdot}OEt){\cdot}C_6H_4{\cdot}COOH$, in colourless needles melting at 237°. That the ethylic group in this compound is attached to the hydroxyl and not to the carboxyl, group is shown from the fact that it readily yields an *acetyl* compound, which crystallises from glacial acetic acid in colourless needles melting at 110—111°.

None of the preceding substances are produced by ethylation of tetrabromophenolphthalein by means of ethylic bromide, the only substance formed being a colourless *diethylic* salt melting at 175°, which is, without doubt, the lactone compound  $CO<\begin{matrix}C_6H_4\\O\text{——}\end{matrix}>C(C_6H_2Br_2{\cdot}OEt)_2$.

J. F. T.

A New Yellow Dye derived from Dinitrofluorescein. By Frédéric Reverdin (*Ber.*, 1897, **30**, 332—334).—By the action of ammonia at the ordinary temperature on dinitrofluorescein, a yellow dye is produced which dyes wool from an acid bath a yellow resembling that of tartrazine. The compound is probably an imido-derivative, formed by the replacement of the oxygen atom of the dinitrofluorescein by an imide group.

Other nitro-derivatives of fluorescein behave similarly. J. F. T.

β-Napthyl Propyl Ketone. By G. Perrier (*Bull. Soc. Chim.*, 1896, [3], 15, 322—323. Compare Rousset, this vol., i, 75).—By the action of aluminium on a boiling solution of naphthalene and butyric chloride in carbon bisulphide, the author obtains the compound

$$Al_2Cl_6,2C_3H_7{\cdot}CO{\cdot}C_{10}H_7.$$

It is a crystalline substance melting at 92—95°, decomposing about 97°, very soluble in chloroform and carbon bisulphide, and slightly so in light petroleum. Absolute alcohol and water decompose it with formation of β-naphthyl propyl ketone. The author has also obtained two benzoylanthracenes, two *benzoylphenanthrenes*, a *benzoylacenaphthene*, a *benzoylfluorene*, a *butyryldiphenyl*, a *benzoylretene*, and certain acetophenolenes.

M. W. T.

Action of Nitrous Acid on 2:3′-Naphtholsulphonic Acid. By Rudolf Nietzki and Th. Knapp (*Ber.*, 1897, **30**, 187—190).—A substance which forms red crystals with a golden lustre is often formed by the action of nitrous acid on Schaeffer's β-naphtholsulphonic acid; this compound is best prepared by the action of fuming nitric acid on the sulphonic acid at a low temperature, when it is obtained as a brittle mass, with a beetle-green lustre. It has the formula

$$C_{20}H_{13}NS_2O_8 + H_2O$$

and is probably an indophenol derived from β-naphthaquinone,

$$SO_3H{\cdot}C_{10}H_5O{:}N{\cdot}C_{10}H_5(OH){\cdot}SO_3H \ [N : O : SO_3H = 1 : 2 : 3' \text{ and } N : OH : SO_3H = 1 : 2 : 3].$$

It gives red solutions with acids and yellow with alkalis, but in both cases the colours soon change. Reducing agents convert it into a colourless compound, from which, however, the original substance cannot be recovered by oxidation. When heated with aniline, it yields a *compound*, $NPh{:}C_{10}H_5(SO_3H){:}N{\cdot}C_{10}H_5(SO_3H){\cdot}NHPh$, which crystallises in small, yellowish-brown needles containing $1H_2O$. A. H.

Ethereal Oil of Bucco Leaves. By IWAN L. KONDAKOFF [with BIALOBRZESKI] (*J. pr. Chem.*, 1896, [2], **54**, 433—442. Compare Shimoyama, Abstr., 1888, 1205).—From this oil, the following substances were isolated. (1) A stearoptene, $C_{10}H_{16}O$, of phenol-aldehydic character, already described, and named diosphenol. This melts at 82°, and boils at 112° under 14 mm. pressure, and at 232° under 755 mm., but it undergoes partial decomposition at the latter temperature; it has a faint odour, resembling that of thymol. It restores the colour to magenta that has been decolorised with sulphurous acid, gives a silver-mirror with ammoniacal silver solution, yields a *phenylhydrazone* which can be obtained at a low temperature in yellowish crystals, readily deliquescing at the ordinary temperature, and an *oxime*, $OH{\cdot}C_9H_{14}{\cdot}CH{:}NOH$, which crystallises in groups of six-sided plates, and melts at 156°. Moist silver oxide oxidises it to an acid which does not crystallise and forms amorphous salts. This constituent of the oil was separated by cooling it to $-20°$. It was found possible to separate the residual oil, the so-called elæoptene, into two constituents. (2) One of these is a substance, $C_{10}H_{18}O$, with the properties of a hydroaromatic ketone, and closely resembling menthone. It boils at 207—209° under 757 mm. pressure, and at 97—99° under 20 mm. It has a sp. gr. = 0·9145 at 0°/0°, and 0·8994 at 18·5°/18·5°; its specific rotation is $\alpha_D = -6{\cdot}12°$. It yields an *oxime*, $C_{10}H_{18}{:}NOH$, which boils at 140—143° under 20 mm. pressure, at 130—133° under 12 mm., has a sp. gr. = 0·9763 at 0°/0°, and 0·9627 at 18·5°/18·5°; its specific rotation is $\alpha_D = +12{\cdot}7°$. With bromine, it yields a liquid compound, $C_{10}H_{17}BrO,Br_2$, which decomposes spontaneously with evolution of hydrogen bromide. (3) The second constituent of the elæoptene is a hydro-aromatic hydrocarbon, $C_{10}H_{18}$; this boils at 174—176° under 762 mm. pressure, at 65—67° under 14 mm., has a sp. gr. = 0·8802 at 0°/0°, and 0·8648 at 18·5°/18·5°; its specific rotation is $\alpha_D = +60{\cdot}20°$. It has an odour resembling that of peppermint; it decolorises 1 per cent. permanganate, and reacts vigorously with bromine. C. F. B.

A Partial Synthesis of Camphor. By ALBIN HALLER (*Bull. Soc. Chim.*, 1896, [3], **15**, 324—327).—The author claims priority over the work of Bredt and Rosenberg (Abstr., 1896, i, 178). M. W. T.

Xanthorrhœa Resins. By K. HILDEBRAND (*Arch. Pharm.*, 1896, **234**, 698—707. Compare Abstr., 1894, i, 47).—Yellow xanthorrhœa resin contains 4 per cent. of free paracoumaric acid, 0·5 of free cinnamic acid, 7 per cent. of paracoumaric acid, and 0·6 per cent. of cinnamic acid combined with tannol, also 1 per cent. of styracin and phenylpropylic cinnamate (?), 0·6 per cent. of parahydroxybenzaldehyde and vanillin, and 80 per cent. of xanthoresinotannol, chiefly in the form of its paracoumarate. The red resin contains no trace of cinnamic acid, but 1 per cent. of free coumaric acid, 2 per cent. of the same acid combined with tannol, 0·6 per cent. of parahydroxybenzaldehyde, and 85 per cent. of erythroresinotannol chiefly as its paracoumarate. *Xanthoresinotannol* $C_{43}H_{45}O_9\cdot OH$, is insoluble in ether, benzene, chloroform, and carbon bisulphide, but readily soluble in alcohol, acetic acid, ethylic acetate, potash, acetone, and phenol. Its *benzoyl* and *acetyl* derivatives were prepared. On distillation with zinc dust, it gave benzene, toluene, phenol, and naphthalene; and on oxidation with nitric acid it yielded picric acid. On treatment with sodium peroxide, it gave a small quantity of paracoumaric acid.

Erythroresinotannol, $C_{40}H_{39}O_9\cdot OH$, also yielded an *acetyl* and a *benzoyl* derivative. On oxidation with nitric acid, it gave picric acid, and on distillation with zinc dust, benzene, and phenol.

J. J. S.

Convolvulin, the Glucoside of Tubera Jalapæ. (Ipomæa Purga Hayne.) By M. HOEHNEL (*Arch. Pharm.*, 1896, **234**, 647—685). —Convolvulin, $C_{54}H_{96}O_{27}$, obtained from *Tubera Jalapæ* by Mayer's method, after purification by repeated solution in alcohol and precipitation with ether, is a pure white, amorphous substance, insoluble in ether, benzene, and water, only sparingly soluble in chloroform, but readily so in alcohol, glacial acetic acid, and ethylic acetate. It melts at 150—155° and readily reduces ammoniacal silver nitrate, but acts slowly with Fehling's solution unless previously hydrolysed. *Tribromoconvolvulin*, $C_{54}H_{93}Br_3O_{27}$, obtained by the action of bromine on an ice-cold solution of convolvulin in acetic acid, is also a white, amorphous powder. It is readily soluble in ether and decomposes on keeping. *Tribenzoylconvolvulin*, which is a white, amorphous substance melting at 125—131°, is readily soluble in alcohol and ether, but insoluble in light petroleum. When acetylated by Liebermann's method (*Ber.*, 1878, 11, 1169) convolvulin yields a *nonacetyl* derivative, $C_{54}H_{87}Ac_9O_{27}$, which could not be obtained in a crystalline form; it is readily soluble in most organic solvents, and melts at 112—115°.

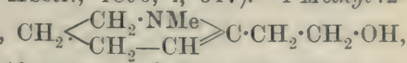
On hydrolysis with barium hydroxide (compare Abstr., 1894, i, 540), the glucoside yields the three acids, methylethylacetic acid, which is volatile with steam, and purgic and convolvulic acids, which are not. *Purgic acid*, $C_{25}H_{46}O_{12}$, is readily soluble in ether, and can thus be separated from convolvulic acid. From 200 grams of convolvulin, the author obtained 25 grams of purgic and 125 grams of convolvulic acid. Purgic acid is a yellowish, hygroscopic substance which is readily soluble in water, alcohol, and ether. It does not reduce Fehling's solution unless previously hydrolysed. Its *barium* salt, $C_{25}H_{44}BaO_{12}$ is an amorphous, hygroscopic powder which is readily soluble in water. *Tribenzoylpurgic acid*, obtained by the Baumann-Schotten method, is a white, amorphous powder readily soluble in alcohol and ether. To convolvulic acid (compare Kromer, Abstr., 1894, i, 540), the author gives the formula $C_{45}H_{80}O_{28}$; it melts at 150—155° and has a sp. rotatory power $[\alpha]_D = -34° 68'$. Its *barium* salt $(C_{45}H_{79}O_{28})_2Ba + 2H_2O$, *calcium* salt, $(C_{45}H_{79}O_{28})_2Ca$, *tetrabenzoyl* derivative, which melts at 115—118°, and *octacetyl* derivative were all prepared.

Purgic acid is slowly hydrolysed by mineral acids or more quickly by superheated steam, the products being an uncrystallisable sugar, a volatile acid, namely, *decenoic acid*, $C_9H_{17}\cdot COOH$, and a non-volatile acid, *hydroxylauric acid*, $OH\cdot C_{11}H_{22}\cdot COOH$. The *silver* and *calcium* salts of the decenoic acid are described, but the amount of acid obtained was not sufficient to determine its actual constitution. Hydroxylauric acid crystallises in small plates, it is insoluble in water and light petroleum, but readily soluble in alcohol and ether. The *silver* salt, *copper* salt, *methylic* salt, and *monobenzoyl* derivate (m. p. 41·5°) are described.

Convolvulic acid is hydrolysed by superheated steam yielding *d*-glucose and *convolvulinolic acid*, $C_{15}H_{30}O_3$; the latter melts at 51·5° (compare Kromer). The *silver*, *barium*, and *ethylic* salts (m. p. 22·5°) are described, as also the reactions of the acid with hydrogen chloride and bromide. Convolvulinolic acid, on oxidation with potassium permanganate or with nitric acid, yields *ipomic acid*, $C_{10}H_{18}O_4$, which is isomeric with sebacic acid, also a valeric acid, probably methylethylacetic acid. (Compare also Taverne, Abstr., 1895, i, 119). J. J. S.

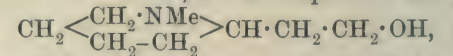
Curcumin. By Giacomo L. Ciamician and Paul G. Silber (*Ber.*, 1897, **30**, 192—195).—Curcumin, when purified by repeated crystallisation, melts at 183°, whereas Jackson and Menke (*Amer. Chem. Journ.*, **4**, 77) give it as 178°; the formula, moreover, is $C_{19}H_{14}O_4(OMe)_2$, and not $C_{14}H_{14}O_4$ as stated by previous observers. The *diacetate*, $C_{19}H_{12}O_2(OMe)_2(OAc)_2$, is prepared by the action of acetic anhydride, and crystallises in large, yellow needles melting at 170—171°. *Dimethylcurcumin*, $C_{19}H_{12}O_2(OMe)_4$, obtained by the action of methylic iodide and methyl alcoholic potash on curcumin, crystallises in golden-yellow needles, melts at 135°, and as it is insoluble in alkalis, probably contains no free hydroxyl groups. With hydroxylamine, curcumin yields a *substance* which melts at 173°, and probably has the formula $C_{21}H_{19}NO_5$; it also reacts with phenylhydrazine, but the product has not yet been obtained pure. A. H.

Synthesis of Tetrahydropyridine Derivatives, and their Conversion into Piperidine Derivatives. By Andreas Lipp (*Annalen*, 1896, **294**, 135—164. Compare Abstr., 1896, i, 317).—1-*Methyl*:2-*hydroxyethyl*-Δ²-*tetrahydropyridine*,



$CH_2<\begin{matrix}CH_2\cdot NMe\\CH_2—CH\end{matrix}>C\cdot CH_2\cdot CH_2\cdot OH$,

is obtained by cautiously adding a 40 per cent. solution of formaldehyde to methyltetrahydropicoline dissolved in water; after 24 hours, the liquid is distilled in a current of steam, the distillate saturated with hydrogen chloride, and evaporated to dryness. The base boils at 199—200° under a pressure of 710 mm., and is a colourless, mobile liquid, with a feebly ammoniacal odour; the sp. gr. = 0·96007 at 0°/0°. The *hydrochloride* and *platinochloride* melt at 155—157° and 200—205° respectively; the *aurochloride* sinters at 110°, melts at 119—121°, and decomposes at 135—140°. The *mercurichloride* separates from water in colourless, lustrous crystals, and incompletely melts at 161—162°, fusion becoming complete at 195—200°; the *picrate* melts at 126—127°, and decomposes at 200°.

1-*Methylpipecolylalkine*,  $CH_2<\begin{matrix}CH_2\cdot NMe\\CH_2-CH_2\end{matrix}>CH\cdot CH_2\cdot CH_2\cdot OH$, [1-*Methyl-2-hydroxyethylpiperidine*], produced when the foregoing base is reduced with alcohol and sodium, boils at 214·5—215·5° under a pressure of 720 mm.; it is a colourless, viscous liquid resembling glycerol, and is not identical with Ladenburg's 1-methylpipecolylalkine, obtained by reducing picolylalkine and introducing a methylic group (Abstr., 1893, i, 426). The *hydrochloride* dissolves very readily in water, and separates in prismatic crystals; the *aurochloride* occurs in two modifications, melting at 72—73° and 127—128° respectively, of which the latter may be converted into the former. The *mercurichloride* melts incompletely at 166—167°, and evolves gas at 190—195°. The base combines with methylic iodide, and the *methochloride* crystallises from alcohol in needles; the *aurochloride* and *platinochloride* of the methochloride melt at 101—102° and 230—235° respectively.

1-Methyl-2-vinylpiperidine is obtained by heating 1-methylpipecolylalkine with concentrated hydrochloric acid for 2 hours at 180—185°, and is identical with the compound described by Ladenburg (*loc. cit.*); the *hydrochloride* crystallises in needles, and the platinochloride melts at 185—186°. The *aurochloride* crystallises in prisms and melts at 58—59°, and the *mercurichloride* melts at 177—178°, decomposing at 200—205°; the *picrate* crystallises in yellow prisms, and melts at 193—194°.

The author explains the discrepancy between the properties of *n*-methylpipecolylalkine prepared by his method and those of Ladenburg's compound, by bringing evidence to show that, when picolylalkine is reduced in alcoholic solution with sodium, a mixture of a primary with a secondary base is produced, owing to the ring being ruptured.

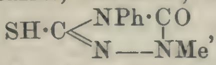
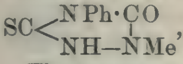
Support is given to Merling's formula for tropine. M. O. F.

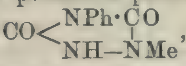
Formation of Pyrazine and its Homologues from Glucose and Ammonia. By P. Brandes and Carl Stoehr (*J. pr. Chem.*, 1896, [2], 54, 481—495).—In repetition of Tanret's experiments (Abstr., 1885, 1047), 6 parts of glucose was heated with 10 parts of 25 per cent. ammonia for 35 hours at 100°, and the product distilled with potash. From the distillate, pyridine, pyrazine, and methylpyrazine were isolated, and identified by their known properties (compare Abstr., 1895, i, 569); the last base is the main product of the reaction; its *ethiodide* crystallises in yellowish needles. A small quantity of a *dimethylpyrazine*, probably $N<\begin{matrix}CH\cdot CMe\\CH\cdot CMe\end{matrix}>N$, was also obtained in the fraction boiling at 147—155°; it melts at 47—48°, is very volatile, and crystallises with great readiness in short, monoclinic prisms [$a:b:c = 0·7678:1:?$]. The yellow *aurochloride*, $C_6H_8N_2,HAuCl_4$, melts and decomposes at 148°, and when warmed with water yields the yellow *salt*, $C_6H_8N_2,AuCl_3$, which melts and decomposes at 144°; the *mercurichloride*, $C_6H_8N_2,6HgCl_2$, and *picrate*, $C_6H_8N_2,C_6H_3N_3O_7$, melting at 175—176°, were also prepared. Tanret's α- and β-glucosine were in reality methyl- and dimethylpyrazine respectively, in spite of the discordance between his boiling points and analyses, and those of the authors. C. F. B.

Derivatives of Methylhydrazine. By WILHELM MARCKWALD and E. SEDLACZEK (*Ber.*, 1896, **29**, 2920—2927).—1 : 4-*Dimethylthiosemicarbazide*, NHMe·CS·NH·NHMe, is formed by the combination of methylthiocarbimide and methylhydrazine, and melts at 138°. 1 : 4-*Methylethylthiosemicarbazide* melts at 84°. The *platinochloride*,

$$C_4H_{11}N_3S,H_2PtCl_6,$$

forms brownish-red crystals.

4 : 1-Phenylmethylthiosemicarbazide, NHPh·CS·NH·NHMe (von Brüning, Abstr., 1890, 23), is not converted by nitrous acid into a thiocarbamide. The *hydrochloride* is very sparingly soluble in hydrochloric acid. When the carbazide is heated at 120°, hydrogen sulphide is evolved, and a mixture of methylhydrazine hydrochloride with a *triazole* derivative, $C_{15}H_{14}N_4S$, is produced; the latter is also formed when phenylmethylthiosemicarbazide is heated with phenylthiocarbimide; it melts at 175° and has basic properties, the *platinochloride* being a yellow, crystalline precipitate. Its constitution has not yet been ascertained. Phenylmethylthiosemicarbazide unites with methylic iodide to form the *hydriodide* of a new base, $C_9H_{13}N_3S,HI$, which melts at 91° and is decomposed by alkalis with formation of methylic mercaptan. The carbazide, moreover, reacts with carbonic chloride to form a *compound*,  $SH\cdot C\Big\langle\begin{array}{l}NPh\cdot CO\\ N\text{——}NMe\end{array}$, which is soluble in alkalis; it melts at 163°, and then becomes changed into an isomeric compound,  $SC\Big\langle\begin{array}{l}NPh\cdot CO\\ NH\text{–}NMe\end{array}$, melting at 212°.

The mercaptan readily reacts with methylic iodide to form a mixture of two hydriodides, one $C_{10}H_{11}N_3OS,HI$, melting at 120°, and the other $(C_{10}H_{11}N_3OS)_2,HI$, at 97°; the second of these is formed when the first is heated with water. These salts are decomposed by strong alkalis, with separation of methylic mercaptan. The mercaptan also reacts with iodine, but the sulphide formed has not been isolated. The isomeric compound, melting at 212°, is also soluble in alkalis, and yields a crystalline *silver salt*, $C_9H_8N_3OSAg$. It does not react with iodine, but when treated with potassium permanganate, it yields the corresponding *oxy-compound*,  $CO\Big\langle\begin{array}{l}NPh\cdot CO\\ NH\text{–}NMe\end{array}$, which forms white crystals, melts at 188°, and has strongly acid properties.

A. H.

Diphenyltetrazoline. By GUIDO PELLIZZARI (*Gazzetta*, 1896, **26**, ii, 430—433).—The author has previously shown that formophenylhydrazide and formamide condense with elimination of $2H_2O$ and formation of 1-phenyltriazole (Abstr., 1895, i, 308); he now shows that, when heated alone, formophenylhydrazide condenses with itself in a similar manner, yielding *n*-diphenyltetrazoline, a compound termed by Ruhemann, who first prepared it, diphenyltetrazine (Trans., 1890, **57**, 50), and by Pinner *n*-diphenylisodihydrotetrazine. The author argues in favour of the adoption of the new name as a generic one.

W. J. P.

Sparteine. By FELIX B. AHRENS (*Ber.*, 1897, **30**, 195—200).—The oxygen atom of oxysparteine is probably present in an aldehyde group, since oxysparteine, when heated with dilute hydrogen peroxide at 100°, is converted into an *acid*, the *barium salt* of which is a yellow, hygroscopic powder of the composition $[C_{14}H_{21}(OH)_2N_2COO]_2Ba$, and sparteine itself is converted by similar treatment into dihydroxysparteine, this acid being accompanied by trioxysparteine. The alcoholic function of the oxygen atoms of dihydroxysparteine is shown by the fact that, when heated with hydrochloric acid at 200°, it is converted into a base, $C_{15}H_{24}N_2$, identical with that obtained by the action of bleaching powder on sparteine. When oxysparteine is treated at the ordinary temperature with 3 per cent. hydrogen peroxide for a considerable time, two products are formed in addition to the acid already described. Of these, the *acid*, $C_{10}H_{16}NO_2 + 3H_2O$, separates from acetone in large, transparent crystals, melts at 287—289°, and is very hygroscopic. It forms readily soluble crystalline *ammonium*, *calcium*, and *zinc salts*, a crystalline *platinochloride* and an *aurochloride*,

$$C_{10}H_{16}NO_2,HAuCl_4,$$

which melts at 194°. The second substance was only obtained in the form of its *picrate*, $C_2H_8NO_3,C_6H_3N_3O_7$ which melts at 227—228° and decomposes at a slightly higher temperature. A. H.

Compounds of Proteid with Nucleic Acid and with Thymic Acid. By T. H. Milroy (*Zeit. physiol. Chem.*, 1896, **22**, 307—326).—The nucleins are divided into the true nucleins, which yield alloxuric bases on decomposition, and the para-nucleins, which do not. Nucleic acid and thymic acid are both precipitants of proteid matter, the precipitate consisting of artificial nuclein, in which the acid is very firmly combined. The properties (solubilities, percentage of phosphorus, behaviour towards digestive ferments) of the artificial nucleins prepared from the several proteids (syntonin, albumoses, &c.) by the use of nucleic acid are very similar to those of the true nucleins, whilst those prepared by the use of thymic acid resemble the para-nucleins; this resemblance, however, is not sufficient to establish identity.

W. D. H.

Oxidation Products of Hæmatoporphyrin and the Composition of Hæmin prepared by Different Methods. By William Küster (*Ber.*, 1897, **30**, 105—110).—Hæmatoporphyrin is formed almost quantitatively by the action of hydrogen bromide dissolved in acetic acid on hæmatin, and is converted by oxidation with chromic acid into the same products as hæmatin, the same two acids, $C_8H_{10}O_5$ and $C_8H_{10}O_6$, being formed (Abstr., 1896, i, 516).

Hæmin hydrochloride, prepared by the author according to Cloëtta's method (Abstr., 1896, i, 660), has the formula $C_{32}H_{31}ClN_4FeO_3$ ascribed to it by Nencki, whereas Cloëtta found for it the formula in which the atomic ratio of nitrogen to iron was 3 : 1. The author ascribes this difference to the action of the concentrated sulphuric acid employed by Cloëtta in its preparation. A. H.

Organic Chemistry.

Preparation of Diethylenic Hydrocarbons. By H. Fournier (*Bull. Soc. Chim.*, 1896, [iii], 15, 400—404. Compare Abstr., 1896, i, 457).—6-*Methyl*-4-*chloro*-1-*heptylene* is obtained by the action of phosphorus pentachloride on isobutylallylcarbinol; it is a colourless liquid, boiling and decomposing at 150—155°, and yields 6-methylhepta-1:3-diene when treated with alcoholic potash.

1:2:3:4-*Tetrabromo*-6-*methylheptane* is prepared by the action of bromine on a solution of the last-named hydrocarbon in chloroform; it is a viscous liquid, which does not solidify at $-15°$.

4-*Chloro*-1-*hexylene* is obtained by the action of phosphorus pentachloride on the corresponding alcohol; it boils and decomposes at 115—120°.

1:3-*Hexadiene* is formed by the action of alcoholic potash on the last-named product, and is a colourless liquid boiling at 72—74°, and of sp. gr. = 0·714 at 12°.

Two stereoisomeric 1:2:3:4-*tetrabromhexylenes* are obtained by treating a solution of 1:3-hexadiene in chloroform with bromine. The one is a crystalline compound melting at 91—92°, and the other a substance which remains liquid at $-20°$. The tetrabromide of 1:4-hexadiene, which might also be produced by removing hydrogen chloride from 4-chlorhexylene, melts at 63—64°. M. W. T.

Constitution of Isoprene. By Wladimir Ipatieff and Nicolaus von Wittorf (*J. pr. Chem.*, 1897, [ii], 55, 1—4).—Isoprene, obtained by distilling Para caoutchouc, boils at 33—38°, and, when treated with an acetic acid solution of hydrogen bromide, yields (1) a compound that is converted by aqueous potassium carbonate into dimethylethylcarbinol, and (2) β-dimethyltrimethylenic dibromide, $CH_3\cdot CMeBr\cdot CH_2\cdot CH_2Br$, boiling at 74—75° under 16 mm. pressure (Abstr., 1896, i, 330). Of these (1) is formed in small amount only; "isoprene" thus contains a little trimethylethylene, but its main constituent, assuming it to be a chain compound (compare following abstract), must be methyldivinyl, $CH_2{:}CMe\cdot CH{:}CH_2$. C. F. B.

Constitution and Synthesis of Isoprene. By Wladimir Ipatieff (*J. pr. Chem.*, 1897, [ii], 55, 4—13).—When β-dimethyltrimethylenic dibromide, made by the addition of hydrogen bromide either to isoprene (preceding abstract), or to dimethylisoallylene, is dropped into strong boiling alcoholic potash, two products are formed. One boils at 120—122°, and appears to be an *ether*, $C_5H_9\cdot OEt$. The other is a hydrocarbon which boils at 32—33° and does not give the reactions of acetylene derivatives, but yet takes up 2 mols. of hydrogen bromide, regenerating the above-mentioned dibromide. It thus contains two double bonds, for the action of alcoholic potash on the dibromide is not likely to have resulted in the formation of a trimethylene ring. It differs, however, from dimethylisoallylene, which boils at 39·5—41°, and must therefore be *methyldivinyl*, $CH_2{:}CMe\cdot CH{:}CH_2$, in which the double bonds are not adjacent. In harmony with this view is the fact that, when treated with hypochlorous acid, it yields a dichlorhydrin; this melts at 81°, and has already been obtained by the addition of hypochlorous acid to isoprene (Favorsky and Mokiewsky, *Chem. Zeit.*, 1895, No. 101). This is further evidence that isoprene itself must be regarded as consisting mainly of methyldivinyl.

C. F. B.

Cyanuric Chloride. By Paul Lemoult (*Compt. rend.*, 1896, **123**, 1276—1278).—Cyanuric chloride was prepared by the action of chlorine on a well cooled solution of dry hydrogen cyanide in chloroform, and purified by repeated sublimation. Its vapour is readily decomposed by water vapour, and hence it must be kept in well-stoppered bottles in a carefully dried atmosphere. Its heat of combustion is 293·7 Cal. at constant volume, and 292·9 Cal. at constant pressure, its heats of formation being respectively +107·1 Cal. and +107·9 Cal. The polymerisation of three molecules of cyanic chloride to form one molecule of cyanuric chloride develops +189·05 Cal., but notwithstanding the large development of heat, the spontaneous change takes place very slowly, especially if the cyanic chloride is pure. The numbers given explain the large development of heat that accompanies the action of chlorine on hydrocyanic acid, and the considerable development of heat in the preparation of cyanuric chloride by the action of phosphorus pentachloride on cyanuric acid. It is noteworthy, however, that the substitution of hydroxyl for chlorine develops considerably less heat than in the case of phosphoryl chloride. Unlike cyanic chloride, cyanuric chloride is comparatively stable in presence of liquid water even at its boiling point.

C. H. B.

Polymerisation of some Cyanic Compounds. By Paul Lemoult (*Compt. rend.*, 1897, **124**, 84—86).—The values given in the preceding paper are incorrect, because in calculating the heat of formation of cyanuric chloride from its elements, account was not taken of the decomposition of the water required for the combustion of the chloride according to the equation $2C_3N_3Cl_3$ sol. + $3H_2O$ liq. + $9O = 6CO_2 + 9HCl + 3N_2$. When the correction is made, the heat of formation of cyanuric chloride becomes +3·9 Cal. at constant volume, and +5·2 Cal. at constant pressure. The formation of the solid chloride by the action of gaseous chlorine on liquid hydrocyanic acid develops +141·7 Cal.; by the action of phosphorus pentachloride on cyanuric acid, +12·9 Cal. The substitution of 3OH for 3Cl in cyanuric chloride develops +53·7 × 3 Cal., which is practically identical with the corresponding value for phosphoric acid. In the direct action of water on cyanuric chloride, the heat developed is +20·1 Cal. (6·7 × 3), somewhat higher than the corresponding value for acetic chloride.

The conversion of liquid cyanogen chloride into solid cyanuric chloride develops +28·7 × 3 Cal.; the conversion of dissolved cyanic acid into dissolved cyanuric acid develops +16·7 × 3 Cal., and the conversion of liquid cyanic acid into solid cyanuric acid will develop approximately +29·4 × 3 Cal. The conversion of cyanamide into melamine develops +15·5 × 3 Cal.

C. H. B.

Aluminium Ethoxide. By HOMER W. HILLYER and O. E. CROOKER (*Amer. Chem. J.*, 1897, **19**, 37—44).—Aluminium ethoxide, which was prepared by Gladstone and Tribe (Trans., 1881, 1 ; 1882, 5 ; 1886, 25) by the action of aluminium foil and iodine on alcohol, is also formed when aluminium is added to a solution of mercuric chloride in alcohol ; stannic chloride gives a similar result, but the product contains aluminium chloride. The ethoxide is a pure white substance melting at 135° and boiling at 235—245° (pressure = 23 mm.).

A. H.

Purification of Phenylglucosazone. By LOUIS HUGOUNENQ (*J. Pharm.*, 1896, [vi], **4**, 447—448).—Phenylglucosazone may readily be purified by washing it in the cold with water, alcohol, and acetone sucessively and then recrystallising from anisoil. The method is preferable to that suggested by Tiemann, and yields the pure osazone melting at 204—205. J. J. S.

Preparation of Pure Starch. By OTTO N. WITT (*Bied. Centr.*, 1896, **25**, 856—857 ; from *Neue Zeits. Zuckerind.*, 1896, No. 11, and (with SIEMENS and HALSKE) *Ger. Pat.*, No. 88447, Class 89, July 23, 1895).—Ordinary starch is for some purposes unsuitable, as the impurities it contains yield products of decomposition some of which are coloured, others of unpleasant odour. Moreover, the cellulose covering of the grains hinders the action of chemical agents.

The following method is used for obtaining pure starch. The starch, mixed with water, is treated with potassium permanganate until the latter is no longer decolorised. The impurities are then all destroyed, whilst manganese peroxide is precipitated on to the starch grains, which are thus coloured brown. To bleach the starch, it is washed, and treated with sulphurous acid. If, however, it is desired to convert the cellulose into oxycellulose (and thus render the starch readily soluble in potash), the starch, after treatment with permanganate, is poured into dilute hydrochloric acid, and continually agitated. The chlorine which is evolved acts on the cellulose. From time to time samples are taken, washed with sulphurous acid, and their solubility in alkali tested. When the conversion into oxycellulose is complete, the starch is collected, treated with aqueous sulphurous acid, washed, and dried. The product has all the properties of pure starch. N. H. J. M.

Precipitation of Carbohydrates by Neutral Salts. By ROBERT A. YOUNG (*Proc. Physiol. Soc.*, 1896—1897, 16—18).—Crystalline carbohydrates are not precipitated by saturating their solutions with neutral salts. Glycogen is completely precipitated by saturating its solutions with magnesium sulphate, sodium magnesium sulphate, and ammonium sulphate at ordinary temperatures, and by sodium sulphate at 33°, at which temperature this salt has its maximum solubility. Starch is precipitated in a similar way. Erythrodextrin is not precipitated by such salts, and so may be readily distinguished from glycogen. Commercial dextrin gives an abundant precipitate on saturation with ammonium sulphate ; this consists partly of soluble starch, partly of one or more intermediate dextrins. Achroodextrin is partly precipitated by ammonium sulphate, and inulin, partly by

magnesium sulphate. The soluble iodine compounds of the carbohydrates, including that of erythrodextrin, are precipitated by saturation with salts, often more readily than the carbohydrates themselves.
W. D. H.

A Correction [Action of Hydroxylamine on Mesityl Oxide]. By Carl D. Harries (*Ber.*, 1897, **30**, 460).—The compound, α-diacetonehydroxylamine, obtained by the action of alcoholic hydroxylamine on mesitylic oxide in the cold (this vol., i, 212), is only produced under exceptional experimental conditions; the compound generally formed is Naegeli's mesityloxime. J. F. T.

Thorium. By G. Urbain (*Bull. Soc. Chim.*, 1896, [iii], **18**, 347—349). —By treating thorium hydroxide, suspended in alcohol with acetylacetone, and subsequently concentrating the solution, the author obtains a compound of the formula $Th(C_5H_7O_2)_4$. It is a crystalline substance, melts at 171—172°, sublimes in a vacuum, is very soluble in ether and ethylenic dibromide, but only slightly so in water.

Under the same conditions, cerium hydroxide forms an insoluble, grey, amorphous substance which appears to have the composition $CeO{\cdot}CH(CO{\cdot}CH_3)_2$.

This reaction serves as a means of separating cerium from thorium.
M. W. T.

Preparation of Pure Ethylidenelactic Acid, and Preliminary Experiments on Distillation in a Vacuum. By Wilhelm A. Dyes (*Chem. Centr.*, 1896, i, 742—743; from *Diss.*, 1895, Heidelberg). —In the experiments on distillation, the author made use of Babo's air-pump, which he prefers on account of the small quantity of mercury required and its simple manipulation. Pure fermentation or ethylidenelactic acid is obtained by removing the water from the ordinary purchasable solution by heating at 60° under a pressure of 1 mm., and distilling the residue, at 0·5 to 1 mm. pressure, from a short-necked distilling flask immersed in a bath of Wood's metal; just before actual boiling begins, a slight liberation of water is noticed. By repeated distillation, a liquid is obtained which boils constantly at 82—85° under a pressure of 0·5 to 1 mm., and leaves scarcely any residue on evaporation. Its density at 25° is 1·23, and its composition corresponds with the formula $C_3H_6O_3$. When strongly cooled, it solidifies to a hard, white, crystalline mass, which melts at 18°, and deliquesces very rapidly in moist air. On distillation, some lactide is formed, but by performing the operation quickly and avoiding superheating, this may be reduced to a minimum. Formation of lactide occurs also on standing in warm air, or in a vacuum over sulphuric acid. A solution containing 95—96 per cent. of acid, and free from anhydride, may, however, be obtained from the commercial solution by first boiling it with water and then drying over sulphuric acid in a vacuum for a limited period. In one case, after boiling with an equal volume of water for 3 hours and drying for 107 hours, a solution containing 96·56 per cent. of acid was obtained, but on continuing the drying for 12 hours longer, the formation of anhydride was found to have reduced the strength of the solution to 96·44 per cent.

By use of the ordinary water vacuum pump, an acid of 95—99·63 per cent. may be prepared. For this purpose, the water is first driven off from a lactic acid solution of density 1·21, by heating at 100° under a pressure of 15 mm. The residue is then distilled by heating in a bath of Wood's metal at 120—121°, the receiver being kept at 90°, in order to remove any water produced by formation of anhydride in the distillate. Under a pressure of 14 mm., the product boiled at 120—121°, at 13 mm. pressure at 119—120°, at 12 mm. at 119°. The sp. gr. of a 98 per cent. acid solution at 25° was found to be 1·23, and of a 93 per cent. solution 1·228. A determination of the sp. gr. is not sufficient to indicate the content of pure acid. Although the commercial lactic acid solution does not lose acidity on standing, a 97 per cent. solution sank to 78 per cent. after remaining at a summer temperature for 6 weeks.

The following boiling points at low pressures were also observed. Lactic acid, about 85° (1 mm.); 91—92° (3 mm.). α-Hydroxyisobutyric acid, 84° (2 mm.). Mannitol, 276—280° (about 1 mm.); 285° (2·5 mm.); 290—295° (3—3·5 mm.). Dulcitol, 275—280° (about 1 mm.); 287—288° (2·5 mm.); 290—295° (3—3·5 mm.).

The following sublimation temperatures are given. Lactide, 95—96° (about 1·5 mm.); about 138° (12 mm.). Succinic acid, 160—165° (2·5—3 mm.); 156—170° (2·2 mm.). Fumaric acid, 165° (1·7 mm.). Maleic anhydride, 45—46° (2 mm.). Mesaconic acid, 139—141° (1·5 mm.); 143—145° (2 mm.). Itaconic acid, 140—141° (about 1 mm.).

E. W. W.

Researches in the Hexamethylene Series. V. The Isomerisation of Hexamethylene. By NICOLAI D. ZELINSKY (*Ber.*, 1897, **30**, 387—391. Compare Abstr., 1895, i, 411).—When hexamethylene iodide is heated with hydriodic acid at 230°, the hydrocarbon which is formed differs from the hexamethylene prepared by the reduction of the iodide with zinc and hydrochloric acid. The latter boils at 79—79·5° (Baeyer) 81—82° (Zelinsky), and has a sp. gr. = 0·7764 at 20°/4°. The hydrocarbon obtained by the use of hydriodic acid, on the other hand, boils at 71·5—72·5°, and has a sp. gr. = 0·7501 at 21°/4°. This substance agrees in its properties with methylpentamethylene, which, when prepared from β-methylpentamethylenic alcohol by means of hydriodic acid, boils at 71·5—72·5°, and has a sp. gr. = 0·7473 at 18°/4°. The hydrocarbon is not at once acted on by bromine, but immediately reacts with concentrated nitric acid. This reaction is not common to any of the polymethylene compounds containing a ring of six carbon atoms, but is given by methylpentamethylene and dimethylpentamethylene. The author therefore concludes that, under the influence of hydriodic acid, the hexamethylene ring is converted into a 5-carbon ring, which, under these circumstances, appears to be more stable than the 6-carbon ring. Hexahydrobenzene, which is formed by the action of hydriodic acid on benzene, also appears to be identical with methylpentamethylene.

A. H.

Parabromometadinitrotoluene and some of its Derivatives. By C. LORING JACKSON and MARTIN H. ITTNER (*Amer. Chem. J.*, 1897, **19**, 1—37. Compare Abstr., 1896, i, 214).—The object of the investigation was to study the behaviour of a bromine atom in the ortho-position between two nitro-groups, the para-position not being occupied by a third negative group. *Parabromometadinitrotoluene* [$Me : NO_2 : Br : NO_2 = 1 : 3 : 4 : 5$] is prepared from dinitrotoluidine, melting at 166°, by treating it with sodium nitrite and hydrobromic acid, the reaction requiring a long time for its completion, on account of the sparing solubility of the base and the diazo-salt in hydrobromic acid. The bromo-derivative crystallises in white prisms or irregular plates, and melts at 118°. Boiling aqueous ammonia converts it into dinitrotoluidine, and boiling aqueous soda into dinitrocresol melting at 85°. Aniline readily converts it into 4 : 3 : 5-*anilidodinitrotoluene*, $C_6H_2Me(NO_2)_2\cdot NHPh$, which crystallises in slender, orange-coloured needles, and melts at 169°; when its solution in benzene is treated with hydrochloric acid and sodium nitrite, *nitrosoanilidodinitrotoluene*, $C_6H_2Me(NO_2)_2\cdot NPh\cdot NO$, is produced quantitatively. This substance crystallises in almost colourless, rhombic plates, and melts and decomposes at 123°.

Bromodinitrotoluene does not appear to react with ethylic sodiomalonate, but gives a brilliant blue compound with sodium ethoxide; this will form the subject of a further communication.

4 : 3 : 5-*Bromodinitrobenzoic acid* is formed when bromodinitrotoluene is boiled with potassium dichromate and sulphuric acid, and in small quantity when chrysanisic acid is treated with hydrobromic acid and sodium nitrite. It crystallises in rhombic plates, is slightly soluble in water, and melts at 181°. The *sodium* salt crystallises with $4H_2O$ in slender needles and is decomposed by boiling with water or alkalis, 3 : 5 : 4-dinitrohydroxybenzoic acid (melting at 245—246°) being formed. The *silver* salt crystallises from dilute alcohol in dull, grey needles. *Ethylic bromodinitrobenzoate* crystallises in short, white needles, and melts at 105°.

4 : 3 : 5-*Anilidodinitrobenzoic acid*, which crystallises in orange-coloured needles, and melts at 239°, yields a *sodium* salt crystallising in orange-red needles with $3H_2O$. The *ethylic* salt forms bright orange-coloured prisms which melt at 154°. No nitroso-compound could be prepared.

Bromodinitrobenzoic acid readily reacts with ethylic sodiomalonate, forming *ethylic* 2 : 6 : 4-*dinitrocarboxyphenylmalonate*,

$$(COOEt)_2CH\cdot C_6H_2(NO_2)_2\cdot COOH,$$

which crystallises in thick, white prisms, and melts at 176°. Silver nitrate added to the ammonium salt produces a white precipitate of *silver ammonium* salt, which probably has the formula

$$(COOEt)_2CAg\cdot C_6H_2(NO_2)_2\cdot COONH_4.$$

Bromodinitrobenzoic acid readily forms a crystalline *salt* with 1 mol. of pyridine, and also combines with 2 mols. of pyridine to form an unstable yellow *compound* which, on repeated crystallisation, is broken up into pyridine bromide and dinitrohydroxybenzoic acid; the latter melts at 245—246°, and not at 235—237° as stated by Salkowski (*Annalen*, 1872, 163, 36). Bromodinitrotoluene reacts with great violence with metaphenylenediamine, forming *amidophenyleneimidodinitrotoluene*, $NH_2\cdot C_6H_4\cdot NH\cdot C_6H_2Me(NO_2)_2$, which crystallises in fan-shaped groups of blunt reddish-brown prisms, and melts at 185°. No crystalline salt can be prepared, and it does not react with a second molecule of bromodinitrotoluene. *Tribromamidophenyleneimidodini-*

trotoluene, $NH_2 \cdot C_6HBr_3 \cdot NH \cdot C_6H_2Me(NO_2)_2$, obtained by the action of bromine water on the foregoing compound, crystallises in brownish-yellow, rhombic plates and melts at 22°.

Tribromanilidodinitrotoluene, $C_6H_2Br_3 \cdot NH \cdot C_6H_2Me(NO_2)_2$, is formed by the action of bromine on anilidodinitrotoluene and crystallises in yellow, rhombic plates melting at 238°. Attempts were made to prepare nitro- and anilido-derivatives of this compound in order to synthesise a substance containing a number of benzene nuclei united by nitrogen atoms, but no crystalline products could be obtained.

4 : 3 : 5-*Chlorodinitrobenzoic acid* is formed when chrysanisic acid is diazotised and the solution heated with cuprous chloride. It crystallises in well-defined prisms melting at about 159°. Bromodinitrobenzoic acid is converted by 11 per cent. aqueous hydrochloric acid at 200° into dinitrophenol $[OH : (NO_2)_2 : = 1 : 2 : 6]$ and another substance, melting at 119°, probably the corresponding bromodinitrobenzene. A. H.

Action of Sulphuric Acid on Anisoil. By WILLIAM B. SHOBER (*Amer. Chem. J.*, 1896, **18**, 858—865).—The author finds that when anisoil is mixed with sulphuric acid and the mixture heated to 92°, anisoildisulphonic acid is invariably formed, the amount increasing with the proportion of sulphuric acid and with the time of heating, but it is not formed at 125° or higher temperatures.

Paranisoilsulphonic acid is always formed, the amount decreasing with increase of temperature, time of heating, and excess of sulphuric acid.

Orthoanisoilsulphonic acid is formed in largest amount when anisoil and sulphuric acid are allowed to react at ordinary temperatures It is not produced, however, if the proportion of sulphuric acid to anisoil is greater than 4 to 1. A. W. C.

Electrolysis of Quinol. By LOUIS LIEBMANN (*Chem. Centr.*, 1896, i, 804; from *Zeit. Elektrotechn. u. Elektrochem.*, 1896, 497—499).—By the electrolysis of quinol, the author has obtained a quantitative conversion into quinhydrone. A more or less concentrated, or a cold, saturated, aqueous solution of quinol is acidified with a few drops of sulphuric acid, and electrolysed under an electromotive force of 12 volts in U-tubes containing electrodes of sheet platinum or cylinders of carbon. Variations of current from 0·02 to 2 ampères do not affect the result, but the current density should be so regulated that no oxygen is given off at the anode. In about 10 minutes, the quinhydrone begins to form at the anode in long, green crystals, which after one crystallisation from alcohol are pure. If, instead of sulphuric acid, nitric acid or a nitrate is added, quinone is formed in very small quantity. The formation of quinhydrone takes place readily with an alternating current, and its production in large crystals renders it a suitable method for the demonstration of such electrolysis. E. W. W.

Phosphates of Diatomic Phenols. By HONORÉ SECRÉTANT (*Bull. Soc. Chim.*, 1896, [iii], **18**, 361—364).—The phenol is heated with excess of phosphorus pentachloride until the mixture becomes viscous; on treating the mass with cold water, a solid residue is obtained, which is purified by recrystallisation from hot water. Analysis showed that the substances had the composition $PO_4(C_6H_4 \cdot OH)_3$.

The *quinol* derivative is a white, crystalline substance, which melts at 149° and boils at very nearly the same temperature. It is very soluble in alcohol, acetic acid, and ether, but insoluble in light petroleum, benzene, and carbon bisulphide.

The *resorcinol* derivative has similar properties, but melts at 75°.

M. W. T.

Aromatic Bisulphides. By P. Genvresse (*Bull. Soc. Chim.*, 1896, [iii], 15, 409—426).—When diphenylene bisulphide is heated with strong sulphuric acid containing 60 per cent. of anhydride in a sealed tube at 100°, sulphurous anhydride is formed, together with a substance soluble in water. On removing the excess of sulphuric acid by barium carbonate, and evaporating the solution, a black residue is left which, after purification by redissolving in water, appears to have the composition $C_6H_4S_2O_3$; this the author regards as *trihydroxyphenylenic bisulphide*, $C_6H(OH)_3S_2$ $[(OH)_3 : S_2 = 1:2:4:3:5]$. It is insoluble in benzene and acetic acid, but soluble in alcohol and water, giving to the solutions a red colour. It forms insoluble substances with all acids and neutral salts, and acts as a dye to silk, wool, or cotton, with or without a mordant.

When a solution of this compound is treated with baryta, a substance is precipitated having the composition $(C_6HS_2O_3)_2Ba$, and on evaporating the aqueous solution, after treatment with carbonic anhydride, a crystalline compound $(C_6HS_2O_3)_2Ba_3$ is obtained; this when boiled with acetic anhydride, gives a *diacetyl* derivative, but if heated at 150° with this reagent, a *triacetyl* derivative is produced. These products were not, however, obtained pure.

When heated with orthotoluidine, metanitraniline, or aniline in presence of nitrous acid, compounds were obtained in which 1 molecule of the amine appeared to enter into combination with 2 molecules of the substance.

Dithionyldiphenylene, $C_6H_4{:}(SO)_2{:}C_6H_4$, melts at 237° (Friedel and Crafts, Abstr., 1889, 242, give it as 241°).

Dinitrodiphenylene bisulphide, obtained by heating a mixture of nitrobenzene, aluminium chloride, and sulphur chloride, is a crystalline substance, of a violet colour, which melts at 112° and decomposes at about 150°. It is very slightly soluble in water, but is soluble in alcohol, benzene, and acetic acid, and is of no use as a permanent dye.

Ditolylenic bisulphide, $C_6H_3Me{:}(S)_2{:}C_6H_3Me$, formed by heating toluene with aluminium chloride and sulphur chloride, is viscous at ordinary temperatures, and boils at 248—250° under 15 mm. pressure. It is insoluble in water, but soluble in alcohol, benzene, toluene, and acetic acid. Its solution in sulphuric acid is of a brilliant violet colour.

Ditolylene disulphone, $C_6H_3Me{:}(SO_2)_2{:}C_6H_3Me$, is obtained by treating a boiling solution of ditolylenic bisulphide with chromic acid. It melts at 184°, and is soluble in acetic acid. Its solution in sulphuric acid is colourless.

M. W. T.

Normal Diazo-compounds. By Arthur R. Hantzsch (*Ber.*, 1897, 30, 339—347).—Bamberger's statement (Abstr., 1896, 299; this vol., i, 217) that normal metallic diazo-salts are scarcely, or comparatively slightly, attacked by sodium amalgam, whereas the iso-salts are readily reduced to hydrazines, is incorrect. The normal salts, if prepared in solution by Schraube's method (pouring a 20—25 per cent. solution of the diazo-chloride, &c., into 40 times its weight of 50 per cent. potassium hydroxide), are readily reduced to hydrazines by sodium amalgam at 0°; and by extracting at once with ether, and evaporating the extract, the hydrazines are obtained in the pure state. The yield is quite as good as with the iso-salt. The reduction may also be effected with zinc dust in alkaline solution, and this agent is further capable of reducing both normal and iso diazo-sulphonates and diazo-cyanides. The solution of normal diazo-salt prepared by Bamberger's method, when it is treated with sodium amalgam, does not lose its power of forming azo-dyes for several hours; during this time, the hydrazine which is at first formed becomes converted into resinous substances. It is formed, however, and it is unaccountable that Bamberger should have overlooked it. The argument for the *structural* isomerism of normal and iso (*syn-* and *anti-*) diazo-salts which he based on their different behaviour towards sodium amalgam is thus devoid of foundation.

Apparently conclusive proof is given that the normal sodium diazo-salt of diazosulphanilic acid prepared by the author was really pure. Bamberger always obtained it mixed with sodium hydroxide, and this is why his determinations of the electrical conductivity gave results which were too high. C. F. B.

Behaviour of Aromatic Diazo-chlorides towards Benzylideneamidoguanidine. By EDGAR WEDEKIND (*Ber.*, 1897, **30**, 444—449).—Thiele has shown (Abstr., 1892, 1295), that amidoguanidine resembles phenylhydrazine in its behaviour towards aldehydes and ketones, and the author now shows that this is also true of its action on diazo-salts.

Guanazylbenzene, $NPh:N\cdot CPh:N\cdot NH\cdot C(NH_2):NH$, is obtained by adding diazobenzene chloride to a cooled solution of benzylideneamidoguanidine in dilute alcohol; it crystallises in orange prisms, and melts at 199°.

According as substitution takes place in the free benzene nucleus or in that introduced by the diazo-salt, the isomerides are distinguished by the symbols I and II.

Meta-II-nitroguanazylbenzene,

$$NO_2\cdot C_6H_4\cdot N:N\cdot CPh:N\cdot NH\cdot C(NH_2):NH,$$

is prepared from metanitrodiazobenzene chloride and benzylideneamidoguanidine, and crystallises in orange needles melting at 206°. *Meta-II-amidoguanazylbenzene* is formed on reducing it with stannous chloride; it crystallises in brownish-yellow needles, and melts at 193°.

Paranitrobenzylideneamidoguanidine crystallises in dark red prisms, and melts at 206°.

Para-I-nitroguanazylbenzene,

$$NPh:N\cdot C(C_6H_4\cdot NO_2):N\cdot NH\cdot C(NH_2):NH,$$

is a brownish-yellow powder which melts at 209°; the solution in concentrated sulphuric acid is first yellow, and then darkens, gradually becoming violet. M. O. F.

Acidyl-nitrosamines. By EUGEN BAMBERGER (*Ber.*, 1897, **30**, 366—384).—Nitrosoacetanilide, and compounds of a more or less similar constitution, exhibit many analogies to diazo-compounds.

Nitrosoacetanilide reacts with benzene, for example, in the following manner—$C_6H_5 \cdot NAc \cdot NO + C_6H_6 = C_6H_5 \cdot C_6H_5 + N_2 + HAc$. With thiophen, it reacts in a similar manner; in one experiment, when the substances were mixed at 0°, and the mixture at once withdrawn from the refrigerator, an explosion took place almost before the mixture had attained the ordinary temperature of the room. In carrying out the reaction, the two substances are mixed at $-10°$, at 0°, or at the ordinary temperature, sometimes in ethereal solution, and are allowed to remain a day or two if action does not take place at once. In some cases, where the reacting substances are not mutually soluble, they are shaken together for some time.

Nitrosoacetanilide with benzene yields diphenyl; with toluene, it yields a mixture of ortho- and para-phenyltolyl; with thiophen, β-phenylthiophen, $C_6H_5 \cdot C_4SH_3$, which melts at 90—90·5° after repeated recrystallisation. With sodium methoxide, it yields methylic benzenediazotate, $C_6H_5 \cdot N_2 \cdot OMe$; with commercial potassium sulphite ("*kalium sulphurosum*"), it gives the diazosulphonate, $C_6H_5 \cdot N_2 \cdot SO_3K$, but with potassium sulphite, freshly prepared by saturating aqueous potassium carbonate with sulphurous anhydride at $-5°$ and then neutralising with solid potassium carbonate, it yields *potassium phenylhydrazinedisulphonate* (following abstract). Ethylic nitrosomethylcarbamate, $COOEt \cdot NMe \cdot NO$, yields α- and β-naphthylic methylic ethers with α- and β-naphthol respectively. Parachloro- and parabromonitrosoacetanilide and nitrosodiphenylcarbamide, $NHPh \cdot CO \cdot NPh \cdot NO$, all react with benzene, yielding parachloro- and parabromo-diphenyl and diphenyl respectively. C. F. B.

Potassium Phenylhydrazinedisulphonate. By Eugen Bamberger and Alexander Meyenberg (*Ber.*, 1897, **30**, 374—378).—This substance, $C_6H_5 \cdot N(SO_3K) \cdot NH \cdot SO_3K$, can be prepared by shaking with a freshly prepared solution of potassium sulphite, either nitrosoacetanilide (compare preceding abstract), potassium benzenediazosulphonate, $C_6H_5 \cdot N{:}N \cdot SO_3K$, or potassium benzeneisodiazotate, $C_6H_5 \cdot N{:}N \cdot OK$; the last method is the most convenient. It crystallises in white needles, and is readily soluble in water; it does not reduce Fehling's solution; when heated with very dilute hydrochloric acid, it yields the monosulphonate, $C_6H_5 \cdot NH \cdot NH \cdot SO_3K$, but with strong hydrochloric acid it gives phenylhydrazine; heating with alkalis converts it first into the diazosulphonate, and finally into potassium sulphanilichydrazosulphonate, $SO_3K \cdot C_6H_4 \cdot NH \cdot NHSO_3K$ (compare von Pechmann, Abstr., 1895, i, 370). C. F. B.

Isomeric Amidines. By Reinhold Walther (*J. pr. Chem.*, 1897, [ii], **55**, 41—48).—*Phenylparatolylmethenylamidine*,

$$NPh{:}CH \cdot NH \cdot C_6H_4Me,$$

melting at 120°, is formed by the action of paratoluidine on diphenylmethenylamidine; the isomeric substance, $C_6H_4Me \cdot N{:}CH \cdot NHPh$, melting at 132°, is obtained when aniline hydrochloride is heated with diparatolylmethenylamidine in alcoholic solution. The yellow platinochlorides of both substances were prepared.

When formotoluidide is heated with aniline in the presence of phosphorus oxychloride, the product melts at 98°, its yellow platinochloride at 207°. Formanilide and paratoluidine yield a product which melts at 102°, its yellow platinochloride at 218°. These two substances are obviously not identical with the two first mentioned, as one would have expected them to be; it is, perhaps, a case of stereoisomerism.

C. F. B.

Paraisobutylphenoxyacetic Acid. By WALTER P. BRADLEY and F. KNIFFEN (*Amer. Chem. J.*, 1897, 19, 70—76).—*Paraisobutylphenoxyacetic acid*, $C_4H_9 \cdot C_6H_4 \cdot O \cdot CH_2 \cdot COOH$, is formed when the sodium salt of paraisobutylphenol is fused with sodium chloracetate. It separates from light petroleum in radiating crystals, and melts at 86·5°. The *barium* and *magnesium* salts are both crystalline; the *methylic* salt could not be obtained crystalline, but is converted by ammonia into the *amide*, which crystallises in snow-white plates melting at 134°. The *anilide* forms long needles and melts at 97°; whilst the *metanitranilide* crystallises in cream-coloured needles and melts at 136—139°. Nitric acid converts the anilide into a *tetranitranilide*, which forms nodular, yellow crystals and melts gradually between 135° and 140°; alcoholic potash hydrolyses it with formation of orthoparadinitraniline, so that two of the nitro-groups are situated in each of the benzene nuclei.

The *orthotoluidide* of the acid crystallises in long, white plates melting at 91°, and the *paratoluidide* forms similar crystals melting at 122°.

The *phenylhydrazide* is colourless, and melts at 171·5°. A. H.

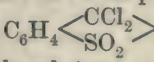
Non-existence of two Orthophthalic Acids. By HENRY L. WHEELER (*Amer. Chem. J.*, 1896, 18, 829—836).—Experiments previously made by Howe (Abstr., 1896, i, 480), by which β-phthalic acid is said to have been prepared, have been carefully repeated with pure materials, but in no case could the acid be obtained.

It is pointed out that Howe's errors are not confined to experimental work, but that the calculated figures for several of his analytical results are wrong, and, moreover, several statements by other authors are inaccurately quoted.

As β-phthalic acid itself could not be obtained, the methods he gives for obtaining its derivatives could not be repeated.

A. W. C.

Two Isomeric Chlorides of Orthosulphobenzoic Acid. By IRA REMSEN (*Amer. Chem. J.*, 1896, 18, 791—794. Compare Abstr., 1895, i, 472).—A *résumé* of recent work on the two isomeric chlorides embodied in the two following abstracts. A. W. C.

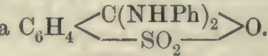
Purification of the Chlorides of Orthosulphobenzoic Acid, and the action of various Reagents on them. By IRA REMSEN and S. R. MCKEE (*Amer. Chem. J.*, 1896, 18, 794—809. Compare Abstr., 1895, i, 472, 473).—Improvements in methods of preparation and separation of the two chlorides are given. The symmetrical compound, $COCl \cdot C_6H_4 \cdot SO_2Cl$ melts at 79—79·5° (uncorr.), not at 76° as previously stated; whereas the unsymmetrical compound,  $C_6H_4{<}{\substack{CCl_2 \\ SO_2}}{>}O$, melts at 21·5—22·5°. When treated with water, both substances yield the same orthosulphobenzoic acid, the chloride of lower melting point being much more rapidly acted on than that of high melting point.

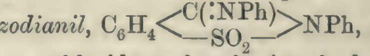
Phenol converts the chloride of high melting point into diphenylic orthosulphobenzoate, a new substance, *phenylic orthosulphaminebenzoate* melting at 131—132° (uncorr.), and an intermediate product which could not be isolated, being produced at the same time. The same substances are obtained from the mixed chlorides or the chloride of lower melting point.

Diphenylic orthosulphaminebenzoate, when treated with ammonia, gives the ammonium salt of benzoicsulphinide, and with hydrochloric acid and alcoholic potash, orthosulphobenzoic acid and its potassium salt respectively.

With resorcinol, both chlorides yield the same sulphonefluorescein, whilst with aniline, the chloride of higher melting point gives the fusible anilide, and that of low melting point a mixture of the fusible and infusible anilides. Ammonia and the chloride of high melting point yield the ammonium salt of benzoicsulphinide, whereas the one of lower melting point is partially transformed into the chloride of higher melting point, and partially into ammonium orthocyanobenzenesulphonate (see below). Both chlorides yield orthobenzoyldiphenylsulphone by the action of benzene and aluminium chloride.

A. W. C.

Relations of the Anilides of Orthosulphobenzoic Acid. By IRA REMSEN and J. R. HUNTER (*Amer. Chem. J.*, 1896, 18, 809—818. Compare Abstr., 1895, i, 472, 473).—By the action of aniline on the mixed chlorides of orthosulphobenzoic acid, two anilides, a fusible and an infusible, are obtained; with benzoic chloride, the infusible anilide yields orthosulphobenzanil and benzanilide. From this and various other reactions which the authors have studied, they conclude that the two aniline residues remain intact in the infusible anilide, which is represented by the formula  $C_6H_4{<}\genfrac{}{}{0pt}{}{C(NHPh)_2}{SO_2}{>}O$.

Orthosulphobenzodianil,  $C_6H_4{<}\genfrac{}{}{0pt}{}{C(:NPh)}{SO_2}{>}NPh$, produced by the action of phosphorus oxychloride or phosphoric anhydride on either anilide, or by the action of phosphorus pentachloride on the infusible anilide, crystallises in brilliant, monoclinic prisms melting at 189·5° (uncorr.). Sodium hydroxide, dilute or concentrated, is without action on it, but when boiled with alcoholic potash or glacial acetic acid, it is converted into the infusible anilide, whilst concentrated hydrochloric acid converts it into orthosulphobenzanil. A. W. C.

Orthocyanobenzenesulphonic Acid. By IRA REMSEN and W. J. KARSLAKE (*Amer. Chem. J.*, 1896, 18, 819—828. Compare preceding abstracts).—*Ammonium orthocyanobenzenesulphonate* is obtained by the action of ammonia on the mixed chlorides of orthosulphobenzoic acid, and on heating this ammonium salt with sodium, potassium, or barium hydroxide, the corresponding well-crystallised sodium, potassium, or barium salt is obtained. All attempts to isolate the free acid proved unsuccessful; barium orthocyanobenzenesulphonate when treated with dilute sulphuric acid yielding orthobenzaminesulphonic acid. *Ammonium orthobenzaminesulphonate* is produced by treating ammonium orthocyanobenzenesulphonate with dilute hydrochloric acid; it crystallises in thin, transparent needles melting at 219—220°

(uncorr.). *Potassium*, *sodium*, *barium*, *calcium*, and basic *lead* salts, prepared by the action of the corresponding hydroxides on ammonium orthocyanobenzenesulphonate, are also described.

Acid ammonium orthosulphobenzoate may be obtained from ammonium orthocyanobenzenesulphonate by heating the latter in sealed tubes with hydrochloric acid. A. W. C.

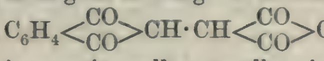
Benzoylcarbinol. By ARNOLD VOSWINKEL (*Chem. Centr.*, 1896, i, 764—765; from *Pharm. Centr.*, H., **37**, 103—105).—In connection with the work of V. Fritz (Abstr., 1896, i, 151), the author describes his own researches. *Benzoylmethylic salicylate*, $OH\cdot C_6H_4\cdot COO\cdot CH_2Bz$, or *salhypnone*, is prepared by the action of sodium salicylate on α-bromacetophenone. It crystallises in long, colourless needles, melts at 113—114°, and is insoluble in water; it reduces Fehling's solution, and on heating with dilute alkalis yields benzaldehyde. It has no special physiological action. The *oxime*, obtained by the action of hydroxylamine hydrochloride in presence of potassium hydroxide, crystallises in needles melting at 97°, whilst the *hydrazone* melts at 133°. On heating to 230—240°, benzoylmethylic salicylate decomposes into phenol, carbonic anhydride, and acetophenone. By the action of dilute hydrochloric acid, crystals are obtained which reduce Fehling's solution and with ferric chloride give a violet coloration; the formula of this new compound is probably $OH\cdot C_6H_4\cdot COO\cdot CH_2\cdot CPh(OEt)_2$.

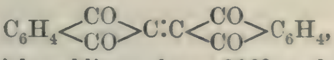
E. W. W.

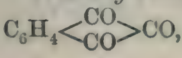
Schiff's Reaction for Aldehydes. By G. URBAIN (*Bull. Soc. Chim.*, 1896, [iii], **15**, 455—456).—It is generally supposed that the restoration of the colour of Schiff's reagent (magenta decolorised by sulphurous acid) by aldehydes is due to the regeneration of the magenta. The author shows that it is really due to the formation of coloured compounds, by the condensation of the aldehyde and the magenta.

M. W. T.

Diphthalylethylene; an Analogue of Indigo in the Indene Series. By VICTOR KAUFMANN (*Ber.*, 1897, **30**, 382—387).—When diketohydrindene is oxidised with dilute hydrogen peroxide or potassium persulphate in alkaline solution, several oxidation products are produced which are analogous to indigo in constitution.

Diphthalylethane,  $C_6H_4{<}\substack{CO\\CO}{>}CH\cdot CH{<}\substack{CO\\CO}{>}C_6H_4$, crystallises from boiling aniline in microscopic, yellow needles, is sparingly soluble in most solvents, and melts and decomposes above 200°. The *potassium* derivative, $C_{18}H_9KO_4$, which is produced in the reaction, is a dark-green, crystalline powder.

Diphthalylethylene (*indenigo*),  $C_6H_4{<}\substack{CO\\CO}{>}C{:}C{<}\substack{CO\\CO}{>}C_6H_4$, forms sparingly soluble red needles, which sublime above 200°, and at the same time partially decompose. It dissolves without decomposition in concentrated sulphuric acid, but is insoluble in aqueous alkalis.

Triketohydrindene (*indanetrione*), which probably has the formula  $C_6H_4{<}\substack{CO\\CO}{>}CO$, was obtained in very small quantity. It crystallises in brownish-yellow plates, and melts and decomposes at 190—206°. A fourth product, also obtained in extremely small quantity, was probably *orthoxalylbenzoic acid* (*2-phenethylonoic-1-methyloic acid*),

$$COOH\cdot C_6H_4\cdot CO\cdot COOH.$$

Attempts to prepare similar compounds from the sodium compound or the bromine derivatives of diketohydrinene proved unsuccessful.

A. H.

Terpenes. By ALBERT REYCHLER (*Bull. Soc. Chim.*, 1896, [iii], 15, 366—376. Compare Abstr., 1896, i, 308).—Details are supplied which relate to the behaviour of terpenes towards trichloracetic acid (*loc. cit.*); the preparation of camphene from pinene hydrochloride and the conversion of that hydrocarbon into isoborneol are also described.

Camphene hydrochloride and isobornylic chloride melt at 149—151° and 150—152° respectively, whilst bornylic chloride melts at 157—159°; the author ascribes to these substances the same structural formula, regarding the two former as identical, whilst bornylic chloride is stereoisomeric with them.

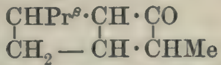
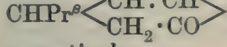
M. O. F.

The Thujone Series. By OTTO WALLACH (*Ber.*, 1897, 30, 423—428. Compare Abstr., 1893, i, 105, 107).—Oxidation of thujone (tanacetone) gives rise to α- and β-thujaketonic (tanacetoketonic) acids (*loc. cit.*); the oxime of the α-modification (m. p. 168°) gives rise to the *compound* $C_{10}H_{16}O_2\colon NOH,HCl$, and the *compound* $C_{10}H_{16}O_2\colon NOH,HBr$, which melt at 128—129° and 176—177° respectively. Whilst alkali hypobromite converts α-thujaketonic acid into Semmler's tanacetogendicarboxylic acid (m. p. 141·5°), the β-acid gives rise to an unsaturated, isomeric *acid*, $C_9H_{14}O_4$, which melts at 113—114°; this observation confirms the author's former conclusion in regarding the β-acid as unsaturated, but the α-acid is saturated, and is so constructed as to yield an ethylene linking under the influence of acids and high temperature.

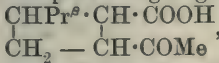
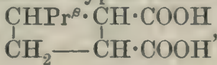
Methylheptylene ketone, $C_9H_{16}O$ (Abstr., 1893, i, 107, 597), obtained by distilling the thujaketonic acids, forms the *semicarbazone* which melts at 143°, and the *benzylidene* derivative, which crystallises in white needles, and melts at 170°; reduction converts the ketone into an alcohol, $C_9H_{17}\cdot OH$, which is oxidised by permanganate to the *glycerol*, $C_9H_{17}(OH)_3$, a syrupy liquid which boils at 160—165° under a pressure of 10 mm. Hot, dilute sulphuric acid converts the glycerol into the *oxide*, $C_9H_{16}O$, which has the odour of pinole, and boils at 160—165°; the *bromo*-derivative, $C_9H_{15}BrO_2$, crystallises from alcohol in white needles, and melts at 124·5°.

Isothujaketonic acid, $C_{10}H_{16}O_3$, is obtained by oxidising isothujone (Abstr., 1895, i, 620) with potassium permanganate; it is a saturated compound, and boils at 142—143° under a pressure of 12 mm., and at 271—273° under atmospheric pressure; the *semicarbazone* melts at 193°, and the *oxime* at 153°. Sodium hypobromite converts isothujaketonic acid into isopropylsuccinic acid with elimination of bromoform.

Thujamenthone, $C_{10}H_{18}O$, more closely resembles menthone than tetrahydrocarvone, being isomeric with both substances. When oxidised with potassium permanganate, it yields the ketonic *acid*, $C_{10}H_{18}O_3$, which forms a *semicarbazone* melting at 174·5°; sodium hypobromite converts the ketonic acid into the dibasic *acid*, $C_9H_{16}O_4$, which melts at 134·5°. On oxidation with chromic acid, thujamenthone gives rise to the ketonic *lactone*, $C_{10}H_{16}O_3$, which melts at 41°; the *oxime* melts at 156°.

Accepting for thujone the formula  $\begin{array}{l}CHPr^{\beta}\cdot CH\cdot CO\\ CH_2 - CH\cdot CHMe\end{array}$ (Semmler, Abstr., 1894, i, 339), the author represents isothujone and isothujaketonic acids by the formulæ  $CHPr^{\beta}<\begin{matrix}CH:CH\\ CH_2\cdot CO\end{matrix}>CHMe$ and $COOH\cdot CH_2\cdot CHPr^{\beta}\cdot CH:CH\cdot COMe$ respectively.

M. O. F.

Tanacetoketonic (Thujaketonic) Acid. By J. C. W. Ferdinand Tiemann and Friedrich W. Semmler (*Ber.*, 1897, **30**, 429—443. Compare foregoing abstract).—α-Tanacetoketonic (thujaketonic) acid,  $\begin{array}{l}CHPr^{\beta}\cdot CH\cdot COOH\\ CH_2 - CH\cdot COMe\end{array}$, arises from tanacetone (thujone) under the influence of a 2 per cent. solution of potassium permanganate, and melts at 74·5°; the oxime melts at 168°, and alkali hypobromite converts the acid into tanacetogendicarboxylic acid,  $\begin{array}{l}CHPr^{\beta}\cdot CH\cdot COOH\\ CH_2 - CH\cdot COOH\end{array}$, which melts at 141—142°.

β-Tanacetoketonic (3-*methoethyl*-2-*heptene*-6-*onoic*) *acid*,

$$COOH\cdot CH:CPr^{\beta}\cdot CH_2\cdot CH_2\cdot COMe,$$

is produced on heating an aqueous solution of the α-acid during a protracted period, and is rapidly formed when the acid is heated at 150° under reduced pressure; it melts at 78°, and the oxime melts at 103—104°.

β-Tanacetogendicarboxylic (3-*Methoethyl*-2-*hexenedioic*) *acid*,

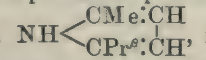
$$COOH\cdot CH:CPr^{\beta}\cdot CH_2\cdot CH_2\cdot COOH,$$

obtained by the action of alkali hypobromite on β-tanacetoketonic acid, crystallises from water, and melts at 116—118° (compare Abstr., 1893, i, 108). *ω-Dimethyllevulinic methyl* (*isobutyrylethyl methyl*) *ketone*, or 2-*methylheptan*-3 : 6-*dione*, $COPr^{\beta}\cdot CH_2\cdot CH_2\cdot COMe$, is produced on oxidising β-tanacetoketonic acid in alkaline solution with a 2 per cent. solution of potassium permanganate; it boils at 102—106° under a pressure of 23 mm., has the sp. gr. = 0·9402 at 20°, and the refractive index, $n_D = 1·4321$, whence the molecular refraction $M = 39·47$. The *oxime* crystallises from water in prisms, and melts at 132°.

ω-Dimethyllevulinic (2-*methylhexan*-3-*onoic*) *acid*,

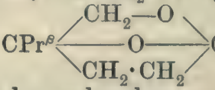
$$COPr^{\beta}\cdot CH_2\cdot CH_2\cdot COOH,$$

arises from the ketone on treating it with alkaline hypobromite, bromoform being eliminated; it melts at 32°, and boils at 145—146° under a pressure of 20 mm. The acid is also produced when β-tanacetogendicarboxylic acid is oxidised with potassium permanganate.

2-*Methyl*-5-*isopropylpyrroline*,  $NH<\begin{matrix}CMe:CH\\ CPr^{\beta}:CH\end{matrix}$, is obtained by heating the diketone with alcoholic ammonia in sealed tubes at 180° for 2 hours; it has the sp. gr. = 0·9051 at 20°, and the refractive index $n_D = 1·4988$, whence the molecular refraction $M = 39·86$.

Tanacetoketone (thujaketone, or 2-*methyl*-3-*metheneheptane*-6-*one*),

$CH_2:CPr^{\beta}\cdot CH_2\cdot CH_2\cdot COMe$, arises from β-tanacetoketonic acid by elimination of carbonic anhydride, and when oxidised with potassium permanganate yields a small proportion of ω-dimethyllevulinic methyl ketone; the chief product, however, is the ketone glycol, 2-*methyl-3-methylolheptan-6-one-3-ol*, $OH\cdot CH_2\cdot CPr^{\beta}(OH)\cdot CH_2\cdot CH_2\cdot COMe$.

Tanacetogen dioxide,  $CPr^{\beta}\left<\begin{array}{c}CH_2{-}O\\ O\\ CH_2\cdot CH_2\end{array}\right>CMe$, is produced on distilling the ketone glycol under reduced pressure, water being suddenly eliminated; it boils at 72—75° under a pressure of 19 mm., has the sp. gr. $=0\cdot9775$ at 20°, and the refractive index $n_D=1\cdot4450$, whence the molecular refraction $M=42\cdot50$. The dioxide has the odour of menthole.

Interesting theoretical considerations are developed in the paper, but they do not lend themselves to condensation. M. O. F.

Geranyl Chloride. By ALBERT REYCHLER (*Bull. Soc. Chim.*, 1896, [iii], 15, 364—366).—The author confirms Barbier's views with regard to the composition of this substance (Abstr., 1893, i, 664), and also the impossibility of removing one molecule of hydrochloric acid from it so as to obtain the compound $C_{10}H_{17}Cl$.

When the compound $C_{10}H_{18}Cl_2$, obtained by saturating geraniol with hydrogen chloride is boiled with excess of water, a product is obtained which is intermediate in composition between $C_{10}H_{18}Cl_2$ and $C_{10}H_{18}O$.

Another attempt to prepare the monochloro-derivative by passing the calculated quantity of hydrogen chloride into geraniol was equally unsuccessful. M. W. T.

Menthol and the Reduction of Menthone. By ERNST O. BECKMANN (*J. pr. Chem.*, 1897, [ii], 55, 14—31).—The *sodium* derivative of natural *l*-menthol was prepared by heating the latter with sodium in an atmosphere of hydrogen. The benzoate and *stearate* were obtained by heating it with the acid anhydrides for several hours at 160—170°; the stearate melts at 39°.

Menthol and menthone can be separated by warming the mixture, in alcoholic solution, with hydroxylamine (? hydrochloride) and sodium hydrogen carbonate, extracting with ether, evaporating down the extract, and again extracting with dilute sulphuric acid. This leaves the menthol behind, but removes menthone oxime, from which the menthone can be regenerated by adding excess of sodium hydroxide together with ice (to avoid rise of temperature), saturating with carbonic anhydride, and extracting with ether. This method of separation does not cause any transformation into optical isomerides.

When menthone is reduced with sodium in alcoholic solution, menthol alone is formed, excess of nascent hydrogen being present. If a solvent is used which gives off no hydrogen when treated with sodium, such as ether, some *menthonepinacone*, $C_{20}H_{38}O_2$, is also formed; this melts at 94°, and in 5 per cent. alcoholic solution at 20°, in a 100 mm. tube has a rotation $a_D=-0\cdot48°$. Whether dextro- or lævo-menthone is reduced, and whichever method of reduction is used, the product is always a mixture of menthols, and is pronouncedly lævorotatory. From this mixture, by forming the benzoates, natural *l*-menthol can be isolated, and, in addition, an *isomenthol* which melts at 78—81°, and has a feeble specific rotation, $[\alpha]_D = +2°$, in 20 per cent. alcoholic solution. The compound of natural menthol with phenylcarbimide, when hydrolysed with alcoholic sodium ethoxide at 150°, yields some *inactive menthol* melting at 49—51°.

In the reduction of menthol with sodium in ethereal solution, only 1 atom of sodium could be used for each molecule of menthol, this being all that would dissolve; on treating the product with water, a mixture of menthol and menthone in molecular proportion is obtained. The ethereal solution is then dried, and again treated with sodium (1 atom) when a complete reduction to menthol occurs, in accordance with the equation

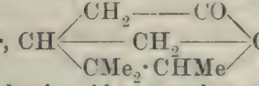
$$C_{10}H_{19}\cdot OH + C_{10}H_{18}O + 2Na = 2C_{10}H_{19}\cdot ONa.$$

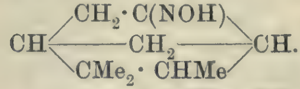
To ensure complete reduction, however, a third treatment with sodium is resorted to.

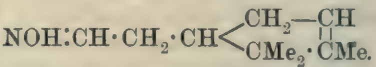
Stearic anhydride can be prepared conveniently by suspending the dry sodium salt of commercial stearic acid in benzene, adding the calculated quantity of phosphorus oxychloride, filtering from the sodium chloride formed, and evaporating the benzene. C. F. B.

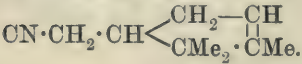
Borneol and the Reduction of Camphor. By ERNST O. BECKMANN (*J. pr. Chem.*, 1897, [ii.], **55**, 31—40).—When camphor is reduced with sodium in boiling alcoholic solution (ethylic or amylic alcohol, or phenol) much more borneol than isoborneol is formed; the boiling point of the solution has little influence. In solution in ether, light petroleum, and cold or boiling toluene, almost as much isoborneol as borneol is formed; the amounts of these present is calculated from the specific rotation of the mixture, that of the pure components being known.

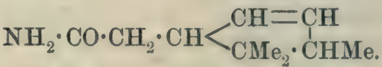
C. F. B.

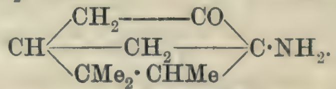
Camphor, III. and IV. By J. C. W. FERDINAND TIEMANN (*Ber.*, 1897, **30**, 321—331, 404—422. Compare this vol., i, 161, 199).—*Isoamidocamphor*,  $CH\left\langle\begin{matrix} CH_2 & — & CO \\ & CH_2 & \\ CMe_2 & \cdot & CHMe \end{matrix}\right\rangle C\cdot NH_2$, is obtained by adding concentrated sulphuric acid to camphoroxime suspended in water, extracting the diluted liquid with ether in order to remove campholenonitrile, and finally rendering alkaline with caustic soda; it is more conveniently prepared by treating camphoroxime with twice its weight of hydriodic acid (sp. gr. = 1·96). It crystallises in prisms, and melts at 39° to an oil which boils at 120°, 133—135°, and 254°, under pressures of 10 mm., 25 mm., and 760 mm., respectively; the base is optically inactive, and is indifferent towards ammoniacal silver and Fehling's solutions. The *benzylidene* and *benzoyl* derivatives melt at 98° and 128° respectively, the *hydrochloride* at 89°, and the *oxalate* at 145°; the *platinochloride* forms bright yellow crystals, and the *aurochloride* dissolves in ether, and crystallises in reddish-yellow leaflets. *Dimethylisoamidocamphor* crystallises in needles and boils at 268—274°; the *hydrochloride* melts at 140°, the *platinochloride* crystallises in yellow needles, and the *hydriodide* forms colourless, lustrous leaflets. When an aqueous solution of isoamidocamphor hydrochloride is heated almost at the boiling point, β-campholenamide is produced, but if the application of heat is maintained for some time, dihydrocampholenolactone is formed. The saturated character of the base, and the resemblance which its chemical and physical properties bear to those of amidocamphor, seem to indicate the existence of a double ring in the former compound, and the author represents its production from camphoroxime by the following steps.

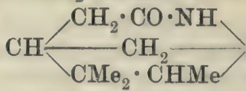
1. 
$CH\left\langle\begin{array}{c}CH_2\cdot C(NOH)\\ CH_2\\ CMe_2\cdot CHMe\end{array}\right\rangle CH.$

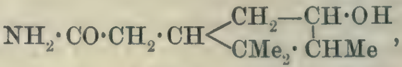
2. 
$NOH{:}CH\cdot CH_2\cdot CH<\begin{array}{l}CH_2-CH\\ CMe_2\cdot CMe.\end{array}$

3. 
$CN\cdot CH_2\cdot CH<\begin{array}{l}CH_2-CH\\ CMe_2\cdot CMe.\end{array}$

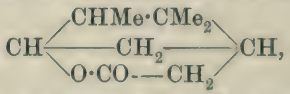
4. 
$NH_2\cdot CO\cdot CH_2\cdot CH<\begin{array}{l}CH=CH\\ CMe_2\cdot CHMe.\end{array}$

5. 
$CH\left\langle\begin{array}{c}CH_2-CO\\ CH_2\\ CMe_2\cdot CHMe\end{array}\right\rangle C\cdot NH_2.$

Dihydrocampholenimide,  $CH\left\langle\begin{array}{c}CH_2\cdot CO\cdot NH\\ CH_2\\ CMe_2\cdot CHMe\end{array}\right\rangle CH$, is obtained by distilling isoamidocamphor under atmospheric pressure in such a manner that the substance is slightly superheated; it crystallises in white needles, melts at 108°, and boils at 266°. The prolonged action of cold mineral acids eliminates ammonia, and gives rise to dihydrocampholenolactone, whilst boiling, concentrated alkalis convert the substance into β-campholenamide.

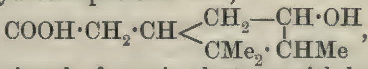
Hydroxydihydrocampholenamide,  $NH_2\cdot CO\cdot CH_2\cdot CH<\begin{array}{l}CH_2-CH\cdot OH\\ CMe_2\cdot CHMe\end{array}$, is the intermediate product in the conversion of dihydrocampholenimide into β-campholenamide, and is obtained by keeping isoamidocamphor in the moist condition during several months; it sublimes without undergoing decomposition, and melts at 184°.

The *compound*, $C_{10}H_{17}NO_2$, is obtained by the action of hydroxylamine on isoamidocamphor hydrochloride in aqueous solution; it crystallises from alcohol in white prisms, and melts at 165°. When isoamidocamphor is treated with boiling water, ammonia is eliminated, and dihydrocampholenolactone produced; the latter substance is also formed when dimethylisoamidocamphor is treated with boiling water, dimethylamine being set free. Isoamidocamphor hydrochloride, on distillation, yields ammonium chloride and an oil which boils at 230—243°.

Dihydrocampholenolactone,  $CH\left\langle\begin{array}{c}CHMe\cdot CMe_2\\ CH_2\\ O\cdot CO-CH_2\end{array}\right\rangle CH$, arises from camphoroxime in varying quantity whenever the substance is treated with concentrated acids. It is obtained in almost quantitative amount when the oxime is decomposed with moderately concentrated sulphuric acid, the liquid diluted with water, and then boiled for some time. In this change, α-campholenonitrile is first produced, and passes immediately into the β-modification, which is hydrolysed to β-campholenamide. Condensation converts the amide into isoamidocamphor, from which, in acid solution, ammonia is eliminated, giving rise to dihydrocampholenolactone. Both campholenic acids are rapidly converted into the lactone, when treated with boiling, concentrated hydrochloric acid. The action of alcoholic and aqueous alkalis, however, is less decisive, and hydroxydihydrocampholenic acid forms an intermediate product.

It invariably happens that dihydrocampholenolactone, when prepared from camphoroxime, is contaminated with the campholenic acids, which are best removed by passing ammonia into an ethereal solution of the lactone; the filtered liquid is then agitated with dilute sulphuric acid, and the lactone, after removing the ether, distilled under reduced pressure. Dihydrocampholenolactone melts at 30° to a colourless oil, which boils at 139°, under a pressure of 18 mm., and at 256° under atmospheric pressure; it has the sp. gr. = 1·0303, and refractive index, $n_D = 1\cdot46801$, whence the molecular refraction $M = 45\cdot79$. The lactone is optically inactive, and the activity displayed by Béhal's preparation must be attributed to the presence of α-campholenic acid.

Syn-Hydroxydihydrocampholenic acid,



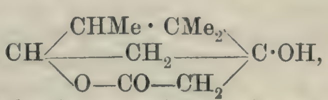
$$\mathrm{COOH\cdot CH_2\cdot CH}<\begin{matrix}\mathrm{CH_2-CH\cdot OH}\\ |\\ \mathrm{CMe_2\cdot CHMe}\end{matrix},$$

obtained by hydrolysing the foregoing lactone with boiling caustic soda, crystallises from ether on the addition of petroleum in slender, white needles, melting at 105°; when heated above the melting point, water is eliminated from the acid, and even at ordinary temperatures, the substance gradually passes into the lactone. The *ammonium* salt melts at 138°, the *sodium* salt does not melt below 250°, and the *basic sodium* salt crystallises from a mixture of alcohol and ether, and melts at 89°.

Anti-Hydroxydihydrocampholenic acid is produced when pinonic acid is heated with concentrated alcoholic potash for several hours at 280°; it crystallises in white needles having the appearance of the *syn*-modification, and melts at approximately the same temperature as that substance, but water is not eliminated under the influence of heat, and the acid may be distilled without undergoing decomposition.

Syn-Hydroxydihydrocampholenic acid is slowly attacked by a boiling solution of potassium permanganate, yielding acetic, oxalic, and isobutyric acids, along with methyl isopropyl ketone; the same products are obtained on oxidising dihydrocampholenolactone in alkaline solution.

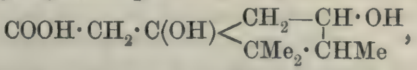
β-Hydroxydihydrocampholenolactone,



$$\mathrm{CH}\begin{matrix}\diagup\mathrm{CHMe\cdot CMe_2}\diagdown\\ -\!\!-\mathrm{CH_2}-\!\!-\\ \diagdown\mathrm{O-CO-CH_2}\diagup\end{matrix}\mathrm{C\cdot OH},$$

is obtained by oxidising dihydrocampholenolactone with a mixture of chromic and sulphuric acids; it crystallises from water, melts at 144°, and boils at 273—275°.

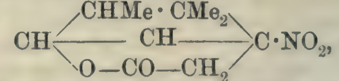
βδ-Dihydroxydihydrocampholenic acid,

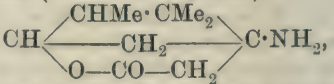


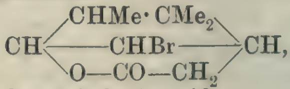
$$\mathrm{COOH\cdot CH_2\cdot C(OH)}<\begin{matrix}\mathrm{CH_2-CH\cdot OH}\\ |\\ \mathrm{CMe_2\cdot CHMe}\end{matrix},$$

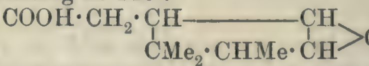
is a highly unstable compound produced on hydrolysing the foregoing lactone, and passes so readily into that substance that no definite melting point can be recorded; according to the quantity of lactone present in the specimen, it melts indefinitely at 91—127°.

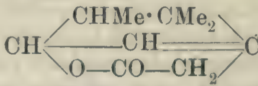
It has been previously stated that the oxidation of dihydrocampholenolactone with chromic acid leads ultimately to isoketocamphoric, isocamphoronic, and terebic acids; this statement must, however, be withdrawn, the mixture of acids in question arising from a specimen of the lactone contaminated with α-campholenic acid.

Nitrodihydrocampholenolactone,  is obtained by the action of dilute nitric acid on dihydrocampholenolactone, and melts at 175°; it was first obtained by Kachler and Spitzer, who described it as nitrocampholenic acid, its lactonic character being recognised by Béhal and Blaise (Abstr., 1896, i, 55).

Amidodihydrocampholenolactone,  arises from the nitro-lactone under the influence of reducing agents; the *hydrochloride* melts at 250°. When this base is treated with nitrous acid, campholenolactone is produced, and not, as might be anticipated, β-hydroxydihydrocampholenolactone; this change is analogous to the conversion of amidocamphor into camphenone.

γ-Bromodihydrocampholenolactone,  obtained by the action of bromine on β-campholenic acid, crystallises from alcohol in prisms melting at 146°.

Campholenoxidic acid,  is produced on hydrolysing the bromo-lactone, and crystallises from a mixture of chloroform and petroleum in needles melting at 128—129°; the *sodium* salt is sparingly soluble in caustic soda. Oxidation converts this acid into 3-dimethylhexen-2-onoic acid.

Campholenolactone,  is obtained on distilling the foregoing acid, or submitting it to the action of hot acids; it melts at 32—34°, and boils at 160—161° under a pressure of 28 mm. The substance is also produced on heating nitrodihydrocampholenolactone with a solution of sodium hydrogen carbonate.

The constitutional formulæ already employed to represent dihydrocampholeno-derivatives are discussed at the termination of the paper.

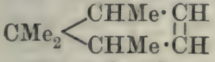
M. O. F.

Campholene. By J. C. W. Ferdinand Tiemann (*Ber.*, 1897, 30, 594—600).—Campholene was first obtained by Delalande on heating campholenic acid with phosphoric anhydride, and subsequently by Kachler, who distilled a mixture of potassium campholate and sodalime; Béhal produced the hydrocarbon by boiling β-campholenic acid with caustic soda (Abstr., 1895, i, 240), this being substantially the method adopted by the author (*loc. cit.*, i, 677).

Campholene, C_9H_{16}, is most conveniently prepared by boiling α- and β-campholenic acids in an apparatus which admits of slight superheating of the material, and by removing the hydrocarbon as it is produced, obviates any lowering of the boiling point of the mixture; it boils at 133—135°, has a sp. gr. = 0·8034 at 20°, and the refractive index $n_D = 1{\cdot}44406$ at 20°, whence the molecular refraction $M = 41{\cdot}00$.

β-Dimethyllevulinic acid, $CH_3\cdot CO\cdot CMe_2\cdot CH_2\cdot COOH$, is obtained on oxidising campholene with a 2 per cent. solution of potassium permanganate at 60°; oxidation with akaline hypobromite eliminates bromoform, and gives rise to unsymmetrical dimethylsuccinic acid. The *semicarbazone* crystallises from hot alcohol, and melts at 190°.

Although, as stated by Guerbet (Abstr., 1894, i, 254), campholene yields hexahydro-ψ-cumene under the influence of concentrated hydriodic acid at 280°, the hydrocarbon cannot be regarded as a derivative of tetrahydro-ψ-cumene; its behaviour on oxidation, and the readiness with which it is obtained from the campholenic acids, point to the formula

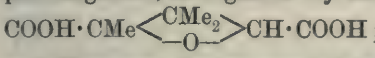


$$\mathrm{CMe_2}\left<\begin{matrix}\mathrm{CHMe\cdot CH}\\ \|\\ \mathrm{CHMe\cdot CH}\end{matrix}\right.$$

as representing its constitution.

The author does not consider that there is sufficient evidence to justify Béhal's view regarding the existence of two isomeric campholenes (Abstr., 1895, i, 240). M. O. F.

Products of Oxidation of Camphoric Acid. By Luigi Balbiano (*Ber.*, 1897, 30, 289—294. Compare Abstr., 1895, i, 552 and 678).—The acid, $C_8H_{12}O_5$, obtained on oxidising camphoric acid with potassium permanganate, is regarded by the author as having the constitution



$$\mathrm{COOH\cdot CMe}\left<\begin{matrix}\mathrm{CMe_2}\\ \mathrm{-O-}\end{matrix}\right>\mathrm{CH\cdot COOH}$$

; this is opposed to the view of Mahla and Tiemann, who represent it by the formula

$$\mathrm{COOH\cdot CHMe\cdot CMe_2\cdot CO\cdot COOH}$$

(Abstr., 1895, i, 679), basing their conclusion on the production of trimethylsuccinic anhydride at 170—220°, and also on the behaviour of the acid towards hydroxylamine and parabromophenylhydrazine. The author has repeated those experiments of Mahla and Tiemann which deal with the latter agent, and finds that the product is not the bromophenylhydrazone, as stated by these investigators, but an additive compound which subsequently loses $1H_2O$, and yields an anhydride devoid of the properties of a hydrazone-acid. Neither hydrochloric nor pyruvic acid eliminates bromophenylhydrazone from this substance, and on heating it at 150—160°, and distilling the product at 220—225° under a pressure of 17 mm., *3-cyano-2-methyl-3-dimethylpropanoic parabromanilide*, $CN\cdot CMe_2\cdot CHMe\cdot CO\cdot NH\cdot C_6H_4Br$, is produced; when this is heated with hydrochloric acid for 6—8 hours at 110—120°, trimethylsuccinic acid, ammonium chloride, and parabromaniline hydrochloride are formed. *Trimethylsuccinic monoparabromanilide*,

$$\mathrm{COOH\cdot CMe_2\cdot CHMe\cdot CO\cdot NH\cdot C_6H_4Br},$$

is obtained by heating the foregoing anilide with the theoretical amount of caustic soda; it crystallises from a mixture of ethylic acetate and petroleum in small, prismatic needles, and melts at 125—126°.

Further evidence against a ketonic formula for the acid $C_8H_{12}O_5$ is afforded by the indifference of the ethylic salt towards aluminium amalgam, parabromophenylhydrazine, and hydroxylamine; the author consequently advocates the oxide formula. M. O. F.

Occurrence of Pine-resin Acids. By EBERHARD RIMBACH *Chem. Centr.*, 1896, i, 756; from *Ber. pharm. Ges.*, 6, 61—64).—The author, on examining the crystals formed on adding water to an alcoholic solution of American colophony, finds that they are not lævorotatory like abietic acid, but strongly dextrorotatory. By recrystallisation from various solvents, conversion of the acid into the insoluble sodium salt, and recrystallisation of this salt, a product is obtained which, on being decomposed by hydrochloric acid, yields crystals of a constant specific rotatory power, $[\alpha]_D = +73\cdot36°$ in chloroform solution, and melting at 210—211°; there is no doubt that this acid is identical with Vesterberg's dextropimaric acid. The molecular weight agrees with the formula $C_{20}H_{20}O_2$. From these facts, it is evident that American colophony may contain, not only abietic acid, but also considerable quantities of dextropimaric acid. In the above case, the latter was accompanied by small quantities of the former. The usual assumption that abietic and dextropimaric acids are characteristic of certain individual resins, must therefore be discarded, and an interchangeable occurrence regarded as more probable.

E. W. W.

Guaiacum Resin. By JOSEF HERZIG and F. SCHIFF (*Ber.*, 1897, 30, 378—380).—The acid of guaiacum resin yields a *diacetate*, $C_{18}H_{18}(OMe)_2(OAc)_2$, and contains two methoxy-groups, whereas Doebner and Lücker have found (this vol., i, 165) that the benzoyl-derivative is a monobenzoate. The authors propose to examine the products of distillation of the resin acid, in order to ascertain the constitution of pyroguaiacin. A. H.

Glucosides of Black and White Mustards. By J. GADAMER (*J. Pharm.*, 1896, [vi.], 4, 462—468; from *Apoth. Zeit.*, 1896, 11, 752).—Potassium myronate (sinigrin) crystallises with $1H_2O$, which it loses at 100° in a vacuum, it then having the composition $C_{10}H_{16}NS_2O_9K$; it undergoes slight decomposition during the drying, and melts at 126—127°. Its solutions are lævogyrate $[\alpha]_D = -15° 13'$. In the decomposition of the glucoside by means of myrosin, water plays a part; a portion of the ferment becomes coagulated by the potassium hydrogen sulphate formed, and is thus rendered useless, but if the acid sulphate is kept neutralised by potash, the decomposition is more complete, although the yield is always some 2 per cent. below the theoretical. The addition of feeble bases, for example, alumina, copper carbonate, or barium carbonate, facilitates the decomposition; an excess of soda or magnesium hydrogen carbonate, however, retards the fermentation.

Some of the secondary products formed are allylic sulphide and cyanide and carbon bisulphide.

Silver nitrate causes a fine crystalline precipitate of the *compound*, $C_3H_5NCS,Ag_2SO_4 + H_2O$, which is the silver salt of an unstable dibasic acid; on adding hydrochloric acid, decomposition ensues, and allylic sulphide and cyanide, together with sulphurous anhydride, are formed. Sulphuric acid acts on allylic cyanide, yielding ammonium sulphate and crotonic acid. On the addition of ammonia to the above-mentioned silver salt, it first dissolves and then a crystalline *compound*, $C_3H_5NCS,Ag_2SO_4,2NH_3$, is deposited. Barium chloride has no action on sinigrin, whereas barium hydroxide brings about complete decomposition. On account of these decompositions, the author regards sinigrin as the potassium salt of an ethereal sulphate derived from the hypothetical imidoxythiocarbonic acid in which the three hydrogen atoms are replaced by SO_2OK, $C_6H_{11}O_5$, and C_3H_5, namely, $C_3H_5{\cdot}N{:}C(S{\cdot}C_6H_{11}O_5)O{\cdot}SO_3K$.

Air-dried sinalbin, the glucoside of white mustard, has the composition $C_{30}H_{42}N_2S_2O_{15} + 5H_2O$; it readily loses $4H_2O$ when kept over sulphuric acid, but only gives up the last molecule when kept over sulphuric acid for 6 weeks. The air-dried compound melts at 83—84°, and the anhydrous compound at 138·5—140°. It is lævogyrate, the rotatory power of the anhydrous compound being $[\alpha]_D = -8° \ 30'$. Under the influence of myrosin, it combines with water, and then yields an essential oil, $C_7H_7O{\cdot}NCS$, sinapin hydrogen sulphate, $C_{16}H_{24}NO_5{\cdot}HSO_4$, and *d*-glucose. On distillation with steam, it yields thiocyanic acid and sulphur. An acid solution of mercuric sulphate yields a compound of definite composition,

$$Hg[S{\cdot}C({:}N{\cdot}C_7H_7O){\cdot}O{\cdot}SO_2{\cdot}O{\cdot}C_{16}H_{24}NO_5]_2,$$

which crystallises in yellowish needles and melts at 155—157°. The author controverts König's statement that white mustard contains sinigrin.

Sinapin, according to Babo and Hirschbrunn, exists in white mustard in two modifications, one of which turns red with ferric salts, whilst the other does not. The author thinks, however, that the latter modification is identical with sinalbin, whereas the former is produced by the decomposition of sinalbin in the course of its preparation by Babo and Hirschbrunn's method. Sinapin exists in black mustard in the form of its *hydrogen sulphate*, which crystallises from water on the addition of sulphuric acid. Its composition is $C_{16}H_{24}NO_5{\cdot}HSO_4 + 2H_2O$, and it melts at 186—188°. The *thiocyanate*, $C_{16}H_{24}NO_3{\cdot}SCN + H_2O$, melts at 178°. It has not been found possible to isolate the base, as it readily dissolves in water and undergoes decomposition. The normal *sulphate* crystallises with $5H_2O$, and undergoes partial decomposition at 100°. The *bromide*, $C_{16}H_{24}NO_5Br + 3H_2O$, and *iodide*, $C_{16}H_{24}NO_5I + 3H_2O$, are both sparingly soluble in water. When treated with barium hydroxide, sinapin is hydrolysed to choline and sinapic acid, $C_{11}H_{12}O_5$; the latter crystallises in yellowish needles and melts at 191—192°. When fused with potash, it yields, according to Remsen and Evale, pyrogallol, but according to the author, hydroxyquinol; it also yields a monacetyl derivative. The author states that, besides the hydroxyl group, it contains two methoxy-groups, and is probably dimethylæsculetic acid. J. J. S.

Compounds from Lichens. By OSWALD HESSE (*Ber.*, 1897, 30, 357—366. Compare Abstr., 1895, i, 298, and Zopf, *ibid.*, 297 and

1896, i, 103).—Usnic acid, $C_{18}H_{16}O_7$, has been obtained from *Usnea barbata*, *U. longissima*, *Parmelia caperata*, *Cetraria pinastri*, *Cladonia rangiferina*, and *Placodium saxicolum*. The so-called β-usnic acid, and other similar acids obtained from these lichens, were mixtures of usnic acid with atranoric acid or atranorin.

Atranorin (Paternò and Oglialoro's atranoric acid) occurs in *Lecanora atra*, *L. sordida var. Swartzii*, *Cladonia rangiformis*, *Physcia parietina*, *Evernia prunastri*, *Parmelia perlata*, and other lichens; it is identical with parmelin. It appears to be the methylic salt, $C_{17}H_{15}O_6\cdot COOMe$, of an acid which could not be isolated, but for which the name of atranoric acid is proposed; when pure it melts at 187—188°. Heating with dilute acetic acid converts it into atranorinic acid, $C_{18}H_{18}O_9 + H_2O$ (not to be confused with Paternò's atranorinic acid), which melts when anhydrous at 157°. Paternò's atranorinic and atraric acids are no other than physciol, which is a phenol containing three oxygen atoms, and physcianin, which is methylic betorcinolcarboxylate; they are also formed when atranorin is heated with glacial acetic acid at 150°. The 'hæmatomminic,' 'hæmatommic,' and 'omminic' acids of Zopf, obtained by heating atranorin with methylic, ethylic, and isopropylic alcohols respectively, are better called the methylic, ethylic, and isopropylic salts of hæmatommic acid, which would have the formula $C_{10}H_9O_4\cdot COOH$; methylphysciol, melting at 142°, however, is formed in small amount at the same time, when it is the ethylic salt that is being prepared.

Chrysocetraric acid has again been prepared from *Cetraria pinastri*, and is now found to melt at 198°. Its composition, and that of its potassium, barium, calcium, lead, and copper salts, and of its acetyl derivative, agree with the formula $C_{18}H_{11}O_5\cdot OMe$. In the mother liquor from this acid, *cetrapic acid*, $C_{17}H_9O_5\cdot OMe$, is found together with usnic acid; it is a yellow substance melting at 147°, and forms a yellow *potassium salt*, $C_{18}H_{11}O_6K + H_2O$, and an *acetyl* derivative which melts at 155°. Cetrapic acid and its acetyl derivative greatly resemble vulpic acid and its acetyl derivative, both in melting point and in other properties, and just as the latter are converted into pulvic acid when hydrolysed, so the former yield a similar acid under the same circumstances. *Cetraria pinastri* contains 1·8 per cent. of these acids; of this amount, one-fourth is cetrapic, one-third chrysocetraric, and the rest usnic acid.

The author further confirms Zopf's statement that *Rhizocarpon geographicum var. lecanorinum* contains rhizocarpic acid together with psoromic acid; the latter acid, however, he finds to be identical with Schunck's parellic acid. Rhizocarpic acid is partially hydrolysed by aqueous sodium carbonate in the cold, yielding yellow *rhizocarpinic acid*, which melts at 170°; when warmed with alkalis, it yields the same substance as vulpic acid does under similar circumstances. The material at the author's disposal did not enable him to execute any analyses, but he is inclined to regard rhizocarpic acid as ethyldipulvic acid, $C_{40}H_{30}O_9$, assigning the formula $C_{38}H_{26}O_9$ to rhizocarpinic acid.

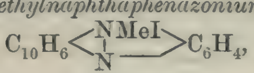
The following are some other acids which he has obtained from various lichens: *Divaricatic acid*, $C_{21}H_{23}O\cdot OMe$, melting at 129°, from

Evernia divaricata. *Ramalic acid,* $C_{16}H_{13}O_6{\cdot}OMe$, melting at 179°, from *Ramalina pollinaria,* in which it occurs together with its isomeride evernic acid. *Sordidic acid,* $C_9H_{10}O_4 + \frac{1}{2}H_2O$, melting when anhydrous at 172°, with evolution of carbonic anhydride, from *Lecanora sordida var. rugosa.* *Thiophanic acid,* $C_{12}H_6O_{12} + H_2O$, melting when anhydrous at 242°, from *Lecanora sordida var. Swartzii*; it is yellow, yields a yellow *potassium salt,* $C_{12}H_3O_{12}K_3 + 8H_2O$, and is converted by strong hydriodic acid into thiophaninic acid, $C_{12}H_6O_9 + H_2O$, which melts when anhydrous at 264°; it is isomeric with mellitic acid, but gives a greenish-black coloration with ferric chloride. The same lichen yields *lecasteric acid,* $C_{10}H_{20}O_4$, melting at 116°, together with its *anhydride,* $C_{10}H_{18}O_3$, which melts at 105°, and is converted into the acid by aqueous sodium carbonate. *Caperatic acid,* $C_{21}H_{35}O_7{\cdot}OMe$, melting at 132°, from *Parmelia caperata,* in which it occurs together with usnic acid and two substances, *caperin* and *caperidin,* which probably both have the formula $C_{24}H_{40}O_2$, and melt respectively at 243° and 262°.

Physcion, $C_{16}H_{12}O_5$ (Rochleder and Heldt's chrysophanic acid), has been obtained from *Gasparrisnia elegans* (= *Squamaria elegans*), *G. murorum,* and *Candelaria concolor,* in all of which it is the only crystallisable constituent. Neither chrysophanic acid proper (the acid of Chinese rhubarb) nor emodin has yet been found by the author in any lichen.
C. F. B.

Relations of the Azonium Bases to the Safranines. By Otto Fischer and Eduard Hepp

(*Ber.*, 1897, 30, 391—402. Compare Abstr., 1893, i, 282—283).—*Methylnaphthaphenazonium chloride,*



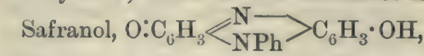
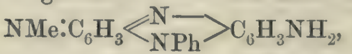
$$C_{10}H_6\left<\begin{matrix}NMeI\\ |\\ N\end{matrix}\right>C_6H_4,$$

crystallises with $1H_2O$ in fan-shaped groups of brownish-yellow needles; the *nitrate* forms long, brownish-red prisms, and the *chromate, aurochloride,* and *platinochloride* are sparingly soluble yellow compounds. The *bromide,* prepared by heating naphthophenazine with methylic bromide, crystallises in concentric groups of orange-coloured needles.

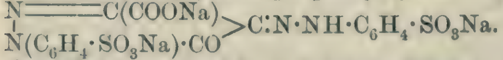
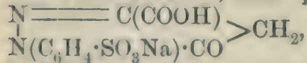
n-Methylrosinduline, $NH{:}C_{10}H_5\left<\begin{matrix}N\\NMe\end{matrix}\right>C_6H_4$, is obtained in the form of its hydrochloride when naphthophenazonium chloride is treated with alcoholic ammonia. The free base crystallises in prisms with a bronze lustre, and gradually decomposes at 100°; it dissolves in sulphuric acid, forming a green solution, which becomes yellowish-red on dilution. The *hydrochloride* crystallises in dark red needles, readily soluble in water; the *nitrate, hydriodide, platinochloride,* and *aurochloride* have all been prepared.

n-Methylrosindone, $O{:}C_{10}H_5\left<\begin{matrix}N\\NMe\end{matrix}\right>C_6H_4$, formed when methylrosinduline is heated with dilute sulphuric acid, crystallises in matted, brick-red needles, which have a golden lustre; it gradually decomposes when heated, even at 100°. It dissolves in sulphuric acid with a cherry-red coloration.

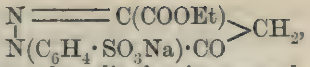
Safraninone (*sym*-amidobenzeneindone), $O{:}C_6H_3\left<\begin{matrix}N\\NPh\end{matrix}\right>C_6H{\cdot}NH_2$, is best prepared by heating phenosafranine hydrochloride with water and sodium acetate at 150°. It is soluble in water, can be diazotised, and forms condensation products with aldehydes. The salicylaldehyde *derivative*, $C_{25}H_{17}N_3O_2$, forms brown crystals with a bluish lustre. When safraninone is heated with dilute alkalis under pressure, safranol is formed. Acetic anhydride converts safraninone or its hydrochloride into a *monacetyl* derivative, which crystallises in slender, red needles melting above 280°, the *hydrochloride* of which forms compact, yellowish-red crystals; under no circumstances is a diacetyl derivative formed.

Safranol,  $O{:}C_6H_3{<}\begin{matrix}N\\NPh\end{matrix}{>}C_6H_3{\cdot}OH$, contains only one hydroxyl group, and yields a monethylic ether when heated with potash and ethylic iodide. The *hydrochloride* crystallises in plates which have a blue iridescence; it is sparingly soluble in hydrochloric acid, and is dissociated by water. *Acetylsafranol* crystallises in red prisms which have a greenish lustre and melt at 265—268°. *Methylphenosafranine*,  $NMe{:}C_6H_3{<}\begin{matrix}N\\NPh\end{matrix}{>}C_6H_3NH_2$, is obtained by the simultaneous oxidation of a mixture of paramethylphenylenediamine and two molecular proportions of aniline. It contains a primary amido-group, and only yields a *monacetyl* derivative, the *hydrochloride* of which forms red crystals with a faint green lustre and is sparingly soluble in alcohol.

These results show that the formulæ proposed by Kehrmann (Abstr., this vol., i, 107) and by Nietzki (this vol., i, 108) for the safranine derivatives cannot be correct, since, according to these, safraninone, safranol, and methylphenosafranine should all yield diacetyl derivatives. The normal safranine salts, moreover, are not to be looked on as azonium salts.
A. H.

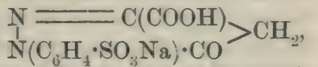
Constitution of Tartrazine. By RICHARD ANSCHÜTZ (*Annalen*, 1896, **294**, 219—243).—The tartrazines are the products of condensation of aromatic hydrazinesulphonic acids with dihydroxytartaric acid, and have been hitherto regarded as osazones; the author, however, adduces evidence in favour of representing them as pyrazolone derivatives, the colouring matter, tartrazine, being the sodium salt of parasulphophenylparasulphophenylhydrazonopyrazolonecarboxylic acid,  $\begin{matrix}N{=\!=\!=}C(COONa)\\ |\\ N(C_6H_4{\cdot}SO_3Na){\cdot}CO\end{matrix}{>}C{:}N{\cdot}NH{\cdot}C_6H_4{\cdot}SO_3Na$. The nomenclature is simplified by referring to this substance as the trisodium salt of *tartrazinic acid*, and parasulphophenylpyrazolonecarboxylic acid  $\begin{matrix}N{=\!=\!=}C(COOH)\\ |\\ N(C_6H_4{\cdot}SO_3Na){\cdot}CO\end{matrix}{>}CH_2$, is called *tartrazinogensulphonic acid*.

Sodium tartrazinate (tartrazine) is obtained by the condensation of phenylhydrazineparasulphonic acid (2 mols.) with dihydroxytartaric acid (1 mol.); its *hydrogen disodium* salt crystallises in small, bright yellow needles on adding sufficient hydrochloric acid to replace one atomic proportion of sodium; *barium tartrazinate* contains $6H_2O$, and forms deep orange-coloured crystals, whilst the *hydrogen barium* salt is anhydrous, and dissolves with difficulty in water.



$$\left.\begin{array}{l}\mathrm{N}=\!=\!=\!=\mathrm{C(COOEt)}\\ |\\ \mathrm{N(C_6H_4{\cdot}SO_3Na){\cdot}CO}\end{array}\right>\mathrm{CH_2}$$

Sodium ethylic tartrazinogensulphonate, is the final product of the action of sodium phenylhydrazineparasulphonate on ethylic oxalacetate, and separates from water as a colourless, crystalline powder; the aqueous solution is acid, and develops a dark violet coloration with ferric chloride. *Silver ethylic tartrazinogensulphonate* forms small, white crystals indifferent towards air and light, and is sparingly soluble in cold water; the *barium* salt is amorphous, and dissolves with difficulty in cold water.



$$\left.\begin{array}{l}\mathrm{N}=\!=\!=\!=\mathrm{C(COOH)}\\ |\\ \mathrm{N(C_6H_4{\cdot}SO_3Na){\cdot}CO}\end{array}\right>\mathrm{CH_2}$$

Sodium hydrogen tartrazinogensulphonate, is obtained by heating the sodium ethylic salt with caustic soda (2 mols.) on the water bath, and treating the liquid with excess of dilute hydrochloric acid; it is almost insoluble in cold water, crystallising in microscopic needles, and develops a violet coloration with ferric chloride. *Silver hydrogen tartrazinogensulphonate* crystallises in colourless prisms, and dissolves with great difficulty in cold water; *barium hydrogen tartrazinogensulphonate* is also crystalline.

Disodium ethylic tartrazinate is produced when diazotised sulphanilic acid is added to sodium ethylic tartrazinogensulphonate, and dissolves with difficulty in cold water; *barium ethylic tartrazinate* is dark yellow, and dissolves sparingly in hot water.

Diphenylizindihydroxytartaric acid,

$$\mathrm{COOH{\cdot}C({:}N{\cdot}NHPh){\cdot}C({:}N{\cdot}NHPh){\cdot}COOH},$$

the osazone of dihydroxytartaric acid, was obtained by Ziegler and Locher (Abstr., 1887, 578), and converted by Knorr into phenylhydrazoneketophenylpyrazolonecarboxylic acid (Abstr., 1888, 724); the former investigators observed that the ammonium salt is somewhat unstable, and on exposure to air yields a deep yellow substance which they regarded as a hydrogen ammonium salt. When the solution of this salt is heated, sparingly soluble, dark red needles are precipitated, and on treating the cold solution with silver nitrate, a dark red substance is formed which acquires a beautiful, cinnabar-red colour on exposure to light; the author finds that these compounds are not hydrogen ammonium diphenylizindihydroxytartrate and silver diphenylizindihydroxytartrimide, as supposed by Ziegler and Locher, but constitute the ammonium and silver salts respectively of Knorr's phenylhydrazoneketophenylpyrazolonecarboxylic acid (compare Wislicenus and Scheidt, Abstr., 1892, 458). M. O. F.

Bases in Fusel Oil. By EUGEN BAMBERGER and ALFRED EINHORN (*Ber.*, 1897, **30**, 224—229).—The authors have established the presence of pyridine and 2 : 5-dimethylpyrazine in fusel oil, and these bases also occur in commercial "pure amylic alcohol"; so that when this solvent is employed in effecting reduction with sodium, piperidine and 2 : 5-dimethylpiperazine are among the products. M. O. F.

Caffeidinecarboxylic Acid. By EMIL FISCHER and OTTO BROMBERG (*Ber.*, 1897, **30**, 219—221).—Caffeidinecarboxylic acid (compare Maly and Andreasch, Abstr., 1883, 1016) crystallises from acetone in long, colourless, prismatic needles, and melts at 160°, when it becomes red, and evolves gas. On heating the acid with phosphorus oxychloride for 3 hours at 115°, caffeine is regenerated. M. O. F.

Methyl-ψ-morphine and its relation to ψ-Morphine and Morphine. By EDUARD VONGERICHTEN (*Annalen*, 1896, **294**, 206—219).—Although it has long been known that morphine is converted into ψ-morphine under the influence of oxidising agents in neutral or alkaline solution, the analogous change does not take place when codeine, the methyl ether of morphine, is submitted to the same treatment; this indifference is also exhibited by diacetylmorphine and methylmorphimethine. By the action of methylic iodide and caustic potash on ψ-morphine, the author has obtained methyl-ψ-morphine, instead of dimethy-ψ-morphine, or ψ-codeïne; as methyl-ψ-morphine contains three hydroxylic groups, the formula ascribed to the tetracetyl derivative of ψ-morphine by Hesse and Dankwortt receives confirmation, and fresh support is given to the view that ψ-morphine arises from the coalescence of two molecules of morphine with elimination of two atoms of hydrogen.

Methyl-ψ-morphine $C_{35}H_{38}N_2O_6$, is obtained in crystals containing $7H_2O$ when ψ-morphine is heated with dilute methylic alcohol, caustic soda and methylic iodide in a reflux apparatus on the water-bath; it is insoluble in hot water, alcohol, dilute caustic soda, ether, and chloroform, becomes anhydrous at 140°, then being very hygroscopic, and blackens at 257—260°. The *hydrochloride* crystallises in colourless, lustrous leaflets containing $4H_2O$; the *platinochloride* is yellow, and the *sulphate* crystallises in white needles which effloresce in the air. The *dimethiodide*, $C_{35}H_{38}N_2O_6,2MeI$, crystallises in prisms, and contains $4H_2O$; ammonia converts this substance into the *basic iodide*,

$$C_{35}H_{38}N_2O_6,MeI,MeOH,$$

which crystallises from hot water in lustrous leaflets containing $6H_2O$. Methyl-ψ-morphine is distinguished from ψ-morphine by its insolubility in cold, normal, caustic soda, which readily dissolves the latter base, the quantity of alkali sufficient for this purpose being less than the amount required on the assumption that ψ-morphine contains two phenolic hydroxyl groups. Whilst morphine combines readily with 1:2:4-chlorodinitrobenzene, yielding dinitrophenylmorphine, ψ-morphine remains almost entirely indifferent towards that agent.

Benzoic chloride converts morphine into the amorphous benzoyl derivative described by Beckett and Wright, ψ-morphine yielding a mixture of the dibenzoyl and tribenzoyl derivatives; the *tribenzoyl* derivative of methyl-ψ-morphine is amorphous, and the *hydrochloride* crystallises in long needles. The *triacetyl* derivative dissolves with difficulty in ether, and the *hydrochloride* crystallises from water in white needles; the *platinochloride* is yellow.

From the indifference of morphine derivatives towards oxidising agents, it is evident that the production of ψ-morphine from morphine depends on the phenolic hydroxyl group of the latter base remaining unsubstituted. M. O. F.

Organic Chemistry.

Conversion of Nitrites into Cyanides. By WILHELM KERP (*Ber.*, 1897, **30**, 610—612).—When sodium nitrite is heated with sodium acetate, the mixture explodes. If, however, the mass be mixed with anhydrous sodium carbonate and then heated, it glows and becomes dark-coloured, evolving hydrogen cyanide; it is then found to contain sodium cyanide, formed according to the equation, $CH_3 \cdot COONa + NaNO_2 = NaHCO_3 + NaCN + H_2O$. About 25 per cent. of the theoretical amount is obtained. Sodium nitrite, when heated with sodium formate, yields nothing but sodium carbonate, whereas with sodium propionate, it deflagrates, and forms small amounts of cyanide. When sodium acetate is heated with potassium nitrate, a violent explosion occurs, and cyanide and cyanate are formed, the same being the case with cream of tartar; in these cases, the formation of cyanide is probably due to the nitrite which is first formed. It appears probable that the first product of the action of the nitrite on sodium acetate is sodium nitrosoacetate, which then decomposes into hydrogen cyanide and sodium hydrogen carbonate: $NO \cdot CH_2 \cdot COONa = HCN + NaHCO_3$.

A. H.

Formation of Diacetylenyl (Butadiine) from Copper Acetylene. By ARTHUR A. NOYES and C. W. TUCKER (*Amer. Chem. J.*, 1897, **19**, 123—128).—Reboul (*Compt. rend.*, **54**, 1229), on passing acetylene into bromine, noticed the formation of a crystalline substance, and Sabanéeff (*Annalen*, **178**, 114) who further investigated this substance, ascribed to it the formula, $C_4H_2Br_6$, and believed it to be hexabromotetramethylene. The authors find that, if pure acetylene, generated from calcium carbide, be passed into boiling bromine, no trace of the solid substance is produced, the true explanation of its origin being that when copper acetylide, made by passing acetylene into ammoniacal cuprous chloride till saturated, is used for generating acetylene, cupric chloride is formed, and this exerts an oxidising action. The hydrocarbon forming the bromide is therefore an oxidation product of acetylene or its copper compound, as represented by the following equations. $2C_2Cu_2 + 2CuCl_2 = C_4Cu_2 + 2Cu_2Cl_2$. $C_4Cu_2 + 2HCl = CH{\vdots}C \cdot C{\vdots}CH + Cu_2Cl_2$. By analysis, and from the determination of its molecular weight by the boiling point method, the substance is proved to have the formula $C_4H_2Br_6$, and is the hexabromide of the unsaturated hydrocarbon diacetylene (diacetylenyl, butadiine). It crystallises in colourless, transparent, orthorhombic plates, melts at 183·5° (corr.), and evolves bromine when heated above its melting point, whilst at 220°, under a pressure of 40 mm., a liquid distils over which partially recombines with the bromine vapour to form the original solid substance.

A. W. C.

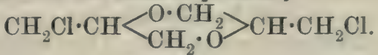
Action of Hydrogen Bromide on Methylbutallylcarbinol. By MAX SCHRAMM (*Ber.*, 1897, **30**, 636—638).—When methylbutallylcarbinol, $CH_2{:}CH{\cdot}CH_2{\cdot}CH_2{\cdot}CHMe{\cdot}OH$, is saturated at 0° with hydrogen bromide, and heated at 70° in closed vessels for 4 hours, a colourless oil is obtained having the odour of oranges; it boils for the most part at 205—211°, and has the composition $C_6H_{12}Br_2$. The substance is probably 2 : 5-dibromohexane, which, according to Demjanoff, boils at 210°; the product from methylbutallylcarbinol, however, is not free from admixture, as it does not solidify at the temperature of the air, although 2 : 5-dibromohexane melts at 38—39°.

Alcoholic potash converts 2 : 5-dibromohexane into $\Delta_{2,4}$-hexinene (2 : 4-hexadiene), a colourless, mobile liquid which boils at 87—89°; this substance is described by Griner as occurring in two modifications, boiling at 77—82° and 82—83° respectively. On adding bromine to a solution of 2 : 4-hexadiene in chloroform, 2 : 3 : 4 : 5-tetrabromohexane is produced; it crystallises in slender, white needles having a faint, camphor-like odour, and melts at 180·5—181°. M. O. F.

Cyclic Ethers of Polyatomic Alcohols. By CARL STOEHR (*J. pr. Chem.*, 1897, [ii], 55, 78—94).—When glycerol is distilled with ammonium phosphate or phosphoric acid, an ether is formed which has a composition and molecular weight corresponding with the formula $C_6H_{10}O_3$; it crystallises from ether in colourless, lustrous tablets, melts at 124—125°, and boils at 209° (corr.). This compound does not appear to contain either the hydroxyl or the carbonyl group, and is very stable towards oxidising agents. With bromine, it combines to form an *additive* compound, which crystallises in red needles and loses bromine over sulphuric acid, leaving the unaltered ether. It also forms, with mercuric chloride, a *compound*, $C_6H_{10}O_3,HgCl_2$, which is sparingly soluble in cold water, and crystallises in thin, lustrous plates melting at 223°. This ether appears therefore to be formed from 2 mols. of glycerol, with the loss of 3 mols. of water. A compound of this character may, however, be formed in several different ways, and its exact constitution has not yet been determined.

When glycerol is distilled with ammonium phosphate and ammonium chloride, or when it is distilled in a current of hydrogen chloride, a substance of the molecular formula $C_6H_{10}O_2Cl_2$ is produced, which is apparently identical with a compound previously obtained by Fauconnier and Sanson (Abstr., 1888, 244). This compound, which the author provisionally names *di-epichlorhydrin*, crystallises in vitreous, monosymmetric prisms, melts at 112—113°, and boils at 232—233°. The chlorine atoms readily undergo displacement, whereas the oxygen atoms appear to be very firmly combined. When the compound is heated with alcoholic potassium iodide at 150°, it yields the corresponding *di-epiiodhydrin*, which crystallises in colourless, brittle needles, melts at 160°, and can be sublimed without decomposition, but decomposes when distilled. Aqueous ammonia converts it into *di-epihydrinamide*, $C_6H_{10}O_2(NH_2)_2$, which is a strong diacid, diprimary base. It boils at 255—256° (uncorr.), almost without decomposition, and crystallises from water in lustrous, monosymmetric tablets, which contain water of crystallisation. It absorbs carbonic anhydride when exposed to the air, and forms crystalline salts. The *hydrochloride* is readily soluble in water; the *platinochloride* crystallises with $2H_2O$; the compound with *mercuric* *chloride* decomposes at 287—288°; the *picrate* decomposes at 260—261°. The *dibenzoyl* derivative crystallises in lustrous, colourless plates, melting at 229°. Nitrous acid converts the base into a dihydroxyl derivative, which has not yet been closely examined.

Di-epichlorhydrin, like the glycerol ether, forms an unstable *additive* compound with bromine, and does not appear to contain either hydroxyl or carbonyl groups. The formula is probably



$$CH_2Cl{\cdot}CH{<}\begin{matrix}O{\cdot}CH_2\\CH_2{\cdot}O\end{matrix}{>}CH{\cdot}CH_2Cl.$$

A. H.

Amount of Pentosan in Cotton Wool. By H. SURINGAR and BERNHARD TOLLENS (*Zeit. angw. Chem.*, 1897, 4—5).—The authors find that cotton wool, when boiled with dilute (4 per cent.) sulphuric acid for 8 hours, yields a certain quantity of sugar, chiefly dextrose. The syrup did not give any definite reaction with phloroglucinol and hydrochloric acid, and they consequently conclude that cotton wool contains but mere traces of pentosans, if any. L. DE K.

Solubility of Cane-Sugar in Dilute Alcohol. By SCHREFELD (*Zeit. anal. Chem.*, 1897, **36**, 196—197; from *Zeit. Zucker. Ind*, **44**, 971).—A table giving the number of grams of sugar, dissolved at 14° by 100 c.c. of a mixture of alcohol and water, for every increment of 5 per cent. of alcohol in the solvent. M. J. S.

Brominated Bases of the Fatty Series. By ALFRED PARTHEIL and H. VON BROICH (*Ber.*, 1897, **30**, 618—621).—Paal (Abstr., 1892, 30) has stated that the trimethyltrimethinammonium bromide, which is formed by the action of alcoholic potash on dibromopropyltrimethylammonium bromide, is in reality a propargyl derivative; this the authors consider to be improbable, because when trimethyltrimethinammonium hydroxide is heated, trimethylamine is formed, along with a second substance which is not propargylic alcohol, but of which the actual constitution has not yet been decided. Trimethyltrimethinammonium hydroxide can be distilled under a low pressure almost without decomposition. It yields a *platinochloride*, $(C_3H_3{\cdot}NMe_3)_2PtCl_6$, which crystallises in slender, brownish-red needles. The *picrate* is sparingly soluble.

Although an attempt to synthesise trimethyltrimethinammonium bromide proved unsuccessful, the following substances were obtained in the course of the experiments. Allylic bromide reacts with 2 mols. methylamine in aqueous solution to form the *hydrobromide* of *methyldiallylamine*, a base which boils at 112°. By the action of methylic iodide on allylamine, *methylallylamine* is obtained as a mobile liquid, boiling at 64—66°. The *nitroso*-compound is a yellow oil which boils at 170—174°. The *platinochloride*, $(C_3H_5{\cdot}NHMe)_2,H_2PtCl_6$, melts at 164°. *Methyldibromopropylammonium bromide*, $C_3H_5Br_2{\cdot}NH_2MeBr$, crystallises in colourless prisms, which melt at 179°. The corresponding *platinochloride* is a crystalline precipitate, and the *aurochloride* forms yellow crystals.

Dimethylallylamine, $C_3H_5{\cdot}NMe_2$, is formed by the action of allylic bromide on dimethylamine in alcoholic solution. The *platinochloride* forms reddish-brown crystals. *Dimethyldibromopropylammonium bromide*, $C_3H_5Br_2\cdot NMe_2HBr$, melts and decomposes at 188—189°. The *chloride* decomposes at 185°; the *platinochloride* forms yellow crystals, and the *aurochloride* reddish-yellow crystals. No definite product of the action of alcoholic potash on the bromide could be isolated.

Allylic bromide unites with triethylamine to form an additive compound, and this combines with bromine to form a *perbromide*,

$$C_3H_5Br_2\cdot NEt_3Br,Br_2,$$

crystallising in reddish-brown needles. On reduction with alcohol, this yields *triethyldibromopropylammonium bromide*, $C_3H_5Br_2\cdot NEt_3Br$, which crystallises in long, hygroscopic needles; the *platinochloride* melts and decomposes at 228—230°; the *aurochloride* is almost insoluble in water. One molecule of alcoholic potash converts the bromide into *triethylmonobromallyammonium bromide*, $C_3H_4Br\cdot NEt_3Br$; this forms white, hygroscopic crystals, and yields a *platinochloride*, which separates in yellowish-red crystals. Two molecules of alcoholic potash, on the other hand, convert the bromide into *triethyltrimethinammonium bromide*, $C_3H_3\cdot NEt_3Br$, which is a white, crystalline powder; the corresponding *platinochloride* is crystalline. A. H.

Behaviour of Diazomethane towards Nitramines. By Otto Degner and Hans von Pechmann (*Ber.*, 1897, **30**, 646—654. Compare Abstr., 1895, i, 493).—The value of diazomethane in determining the structure of tautomeric substances (*loc. cit.*) suggests its employment in attacking the question of the constitution of nitramines. Although, from previous experience of this class of compounds, the production of oxygen ethers might be anticipated, the result is largely influenced by the nature of the complex with which the nitramine group is linked; thus, whilst phenylnitramine yields the oxygen ether almost exclusively, the nitrogen ether preponderates in the case of methylnitramine, nitrocarbamide, and others, nitramide yielding equal quantities of nitrogen and oxygen ethers.

Carbamide is indifferent towards diazomethane, but this agent resolves nitrocarbamide into isocyanic acid and nitramide, according to the equation $O{:}C(NH_2)\cdot NH\cdot NO_2 = O{:}C{:}NH + NH_2\cdot NO_2$, the products being at once converted into the respective methyl derivatives; diazomethane and nitrocarbamide are brought together in ethereal solution, and when the action is at an end, the medium is distilled off at the lowest possible temperature. The ethereal distillate, which has an intense, irritating odour, is without action on Fehling's solution, and does not give the nitramine reaction; it may be shown to contain methylcarbimide by its behaviour towards phenylhydrazine, aniline, and ammonia. The residue contains methylnitramine and dimethylnitramine, along with the oxygen methyl ether of the former (this vol., i, 8).

Methylphenylsemicarbazide, $NHMe\cdot CO\cdot NH\cdot NHPh$, separates in lustrous leaflets when petroleum is added to a mixture of the ethereal distillate with phenylhydrazine; it softens at 148°, and melts at 154—155°. The solution in concentrated sulphuric acid becomes violet with ferric chloride, and the aqueous solution develops a bluish-black coloration with Fehling's solution, the latter being completely reduced on gently heating; nitric acid gives rise to a yellow, crystalline *nitroso*-derivative, and concentrated hydrochloric acid in sealed tubes at 100° resolves the substance into carbonic anhydride, methylamine, and phenylhydrazine.

Methylamidocarbonylazobenzene, $NHMe\cdot CO\cdot N{:}NPh$, is obtained by oxidising methylphenylsemicarbazide in chloroform with mercuric oxide; it crystallises from boiling petroleum in beautiful, long, red needles, and melts at 86°.

Symmetrical phenylmethylcarbamide, $NHMe\cdot CO\cdot NHPh$, is produced when the ethereal solution of methylcarbimide is mixed with aniline and petroleum added; it crystallises from hot water in colourless, lustrous leaflets, and melts at 149—150°. Potassium dichromate added to the solution in concentrated sulphuric acid develops a violet coloration; concentrated hydrochloric acid at 150° resolves it into carbonic anhydride, methylamine, and aniline; *symmetrical parabromophenylmethylcarbamide* crystallises in long, silky needles, and melts at 212°.

When dry ammonia gas is passed into the ethereal solution of methylcarbimide, methylcarbamide is precipitated. Water or alkali carbonates convert the salt into dimethylcarbamide.

Symmetrical methylnitrocarbamide, $NHMe\cdot CO\cdot NH\cdot NO_2$, occurs in the residual oil from which the ethereal solution of methylcarbimide has been distilled; it crystallises from benzene in needles, and melts at 105—106°. Concentrated sulphuric acid decomposes the substance, liberating gas, and ferrous sulphate and sulphuric acid give the nitrosamine reaction; hot potassium carbonate solution liberates methylamine. The *potassium* derivative forms colourless needles, and melts, decomposing at 145°; the *mercuric* derivative is insoluble in water.

Asymmetrical methylnitrocarbamide, $NH_2\cdot CO\cdot NMe\cdot NO_2$, obtained by nitrating methylcarbamide, crystallises from benzene in colourless needles, and melts and evolves gas at 156—157° (compare Thiele and Lachmann, Abstr., 1896, i, 207). The *potassium* derivative crystallises in colourless needles, melting and decomposing at 160°, and the *silver* and *ammonium* derivatives are definite.

It is remarkable that, whilst nitration of ethylcarbamide should give rise to symmetrical ethylnitrocarbamide, as shown by Thiele and Lachmann, the asymmetrical compound should be obtained from methylcarbamide. M. O. F.

Some Metallic Derivatives of Dithioacetylacetone. By Victor Vaillant (*Bull. Soc. Chim.*, [iii], 15, 514—519).—In a previous paper (Abstr., 1895, i, 168), it was shown that when an ethereal solution of dithioacetylacetone, $C_{10}H_{14}S_2O_4$, is treated with sodium, hydrogen is evolved and the compound $C_{10}H_{12}Na_2S_2O_4$ is formed; this substance can, however, be obtained more easily by the action of sodium ethoxide on the ethereal solution of dithioacetylacetone, of which the formula is probably $S_2(CHAc_2)_2$. This sodium derivative can be obtained in yellow needles by crystallisation from alcohol or water, but is insoluble in benzene and ether. It decomposes when heated to 150°, or if its solution is boiled. It is alkaline to phenolphthalein.

The *potassium* derivative resembles the sodium compound. The *magnesium* derivative, $C_{10}H_{12}S_2O_4Mg$, a yellow, crystalline powder, is obtained by the action of an alkaline solution of dithioacetylacetone on a solution of a magnesium salt. The *cobalt* derivative, $C_{10}H_{12}S_2O_4Co$, a rose-coloured salt crystallising in octahedra, is obtained by the same process. It is insoluble in water, but soluble in hot alcohol. The *nickel* derivative, $C_{10}H_{12}S_2O_4Ni$, forms pale green crystals belonging to the quadratic system; it is very soluble in alcohol, but insoluble in water. The copper derivative, $C_{10}H_{12}S_2O_4Cu$ (see Abstr., 1895, i, 168), which is most easily obtained by treating an ethereal solution of dithioacetylacetone with copper acetate, forms bright green crystals, insoluble in water and alcohol, but soluble in chloroform. The *ferric* derivative $(C_{10}H_{12}S_2O_4)_3Fe_2$, obtained by double decomposition, forms minute, deep red crystals, insoluble in water, slightly soluble in alcohol, and very soluble in chloroform. The *aluminium* derivative, $(C_{10}H_{12}S_2O_4)_3Al_2$, forms minute, yellowish-white crystals. Its method of preparation and properties agree with those of the ferric salt. The *uranium* derivative, $C_{10}H_{12}S_2O_4UO_2$, can be obtained by double decomposition, or by shaking a solution of uranium acetate with a chloroform solution of dithioacetylacetone. It crystallises from alcohol in yellow plates. The *bismuth* derivative is a yellow powder, and the *manganese* derivative is a white powder. M. W. T.

The Specific Gravities of Aqueous Solutions of Formic Acid. By George M. Richardson and Pierre Allaire (*Amer. Chem. J.*, 1897, **19**, 149—151).—The authors have determined the specific gravities of mixtures of formic acid and water, and give a table calculated from the results of their observations for every unit by weight of formic acid from 1—100. A. W. C.

Oxidation of the Acids Derived from Fats. By Theod. Marie (*Bull. Soc. Chim.*, 1896, [iii], **15**, 508—510).—The author shows that normal valeric acid is one of the products of the oxidation of stearic acid by potassium permanganate. M. W. T.

Chlorides, Amides, and Nitriles of Cerotic and Melissic Acids. By Theod. Marie (*Bull. Soc. Chim.*, 1896, [iii], **15**, 503—508).—*Cerotic chloride,* obtained by the action of phosphorus pentachloride on the acid, melts at 47°, and reacts readily with water. In order to prepare *cerotamide,* the mixture of cerotic chloride and phosphorus oxychloride is poured, while warm, into ammonia. The amide is soluble in alcohol, but insoluble in ether and water; it melts at 106°. *Cerotonitrile,* obtained by heating the corresponding amide with phosphoric anhydride, is a white, crystalline substance, soluble in alcohol, benzene, ether, &c., but insoluble in water; it melts at 58°.

Melissic chloride, which can be obtained by the same process as cerotic chloride, melts at 60°; *melissamide* melts at 116°, and *melissonitrile* at 70°. These substances closely resemble the corresponding derivatives of cerotic acid. M. W. T.

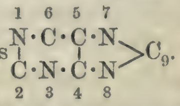
Condensation of Acetone with Ethylic Acetoacetate. By Hermann Pauly (*Ber.*, 1897, **30**, 481—485).—When a mixture of acetone and ethylic acetoacetate is saturated with hydrogen chloride in the cold, and allowed to remain for a time, the product is found to consist of mesityl oxide, a little ethylic isodehydracetate and *ethylic isopropylidenea etoacetate*; the last-mentioned is a yellowish oil, of pleasant odour;

it does not solidify at −20°, and boils at 214—216° (uncorr.); its sp. gr. = 1·001 at 20°/4°. When heated with alkalis or dilute acids, it yields dimethylacrylic acid and acetic acid. Phenylhydrazine converts it into phenylmethylisopropylidenepyrazolone and isopropylidenebisphenylmethylpyrazolone (*Knorr*, Abstr., 1887, 601). A. H.

Substituted Amido-acids, and Imides of Asymmetric Dimethylsuccinic Acid. By Wilhelm Kerp (*Ber.*, 1897, **30**, 613—617). —In view of the fact that Auwers (Abstr., 1896, i, 640), has found the melting points of the anilic acids of asymmetric dimethylsuccinic acid to be about 20° higher than they had previously been found by the author (*Diss. Bonn.*, 1890), the latter has revised the work; and he now finds that the melting points of these substances cannot be exactly determined in the ordinary way, since water is lost during the process, and the temperature, which is observed, depends on the rate of heating, width of tube, &c. The anilic acid crystallises in lustrous plates, and melts at 169° when slowly heated, but at 185—186° if rapidly heated. The orthotolilic acid crystallises in small, lustrous scales, and melts at 146—147° or 154—155°. The paratolilic acid melts at 161—162° or 181° (Auwers 180—185°).

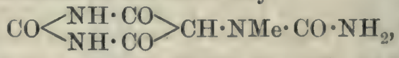
The properties of the anils corresponding with these acids are identical with those given by Auwers. A. H.

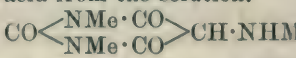
Formation of Carbon Chains. XIII. Diethyldisulphonemethane and Ethylic Diethoxymalonate. By Carl A. Bischoff (*Ber.*, 1897, **30**, 487—491. Compare Abstr., 1896, i, 600).—Diethylsulphonemethane behaves, in various reactions, in a different manner from ethylic malonate, which it resembles in structure, the group SO_2 replacing COO. Thus, when its potassium compound is treated with iodine, it simply forms an iodine substitution derivative, $CI_2(SO_2Et)_2$, and not an analogue of ethylic ethylenetetracarboxylate, $C_2(SO_2Et)_4$. When this di-iodo-derivative, moreover, is treated with ethylic sodiomalonate, it does not bring about the linking of two molecules of the ethylic malonate, but merely yields ethylic ethylenetetracarboxylate and regenerated diethylsulphonemethane. It has been shown by Crum Brown and Fairbairn (*Proc. Roy. Soc. Edinb.*, 1894—1895, 383), that sodium ethylic mercaptan behaves towards ethylic dibromomalonate in a somewhat similar manner, and the author finds that sodium ethoxide in this respect resembles the mercaptan, although, when ethylic dibromomalonate is treated with sodium methoxide, a very small amount of the normal product, *ethylic diethoxymalonate* is formed. This boils at 228°, and crystallises in large prisms melting at 43—44°. The configurations, $C(OEt)_2(COOEt)_2$ and $C(SEt)_2(COOEt)_2$, therefore, seem to be dynamically unfavourable, although ethylic diphenoxymalonate, $C(OPh)_2(COOEt)_2$, and ethylic diacetylmesoxalate $C(OAc)_2(COOEt)_2$, are readily produced. A. H.

Constitution of Caffeine, Xanthine, Hypoxanthine, and Allied Bases. By Emil Fischer (*Ber.*, 1897, **30**, 549—559).—In this paper, the author discusses the constitution of these bases, and considers that, owing to the large increase in the number of derivatives of xanthine and hypoxanthine, the old system of nomenclature is no longer applicable. In his opinion, it is most convenient to consider all these compounds as derivatives of purine ($C_5N_4H_4$), and to number the atoms in its ring nucleus as follows  $\left.\begin{array}{l}\overset{1}{N}\cdot\overset{6}{C}\cdot\overset{5}{C}\cdot\overset{7}{N} \\ \underset{2}{C}\cdot\underset{3}{N}\cdot\underset{4}{C}\cdot\underset{8}{N}\end{array}\right>C_9$. Hypoxanthine is thus 6-oxypurine; uric acid = 2 : 6 : 8-trioxypurine; caffeine = 1 : 3 : 7-trimethyl-2 : 6-dioxypurine; hydroxycaffeine = 1 : 3 : 7-trimethyl-2 : 6 : 8-trioxypurine; guanine = 2-amido-6-oxypurine; adenine = 6-amidopurine. The function of the oxygen atoms, whether hydroxylic or ketonic, is purposely not indicated in the names, owing to the possibility of tautomeric forms existing. J. F. T.

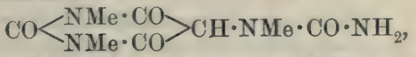
New Synthesis of Uric Acid, Hydroxycaffeine, and Amidodioxypurine. By EMIL FISCHER (*Ber.*, 1897, 30, 559—573. Compare Abstr., 1896, i, 12).—Fusion with oxalic acid converts ψ-uric acid into uric acid (*loc. cit.*), and this effect is also produced by the action of hot, dilute mineral acids; the latter method gives rise to a purer product in more remunerative yield, and is applicable to all substances typified by ψ-uric acid.

In order to obtain uric acid by this process, finely-powdered ψ-uric acid is heated with 500 parts of 20 per cent. hydrochloric acid for 15—20 minutes, the liquid being evaporated to one-fifteenth of its original volume, when uric acid crystallises from the solution. The production of 1 : 3-dimethyluric (γ-dimethyluric) acid from Techow's dimethyl-ψ-uric acid is effected in the same way.

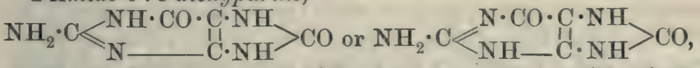
7-*Methyl-ψ-uric acid*,  $CO<\begin{array}{l}NH\cdot CO\\NH\cdot CO\end{array}>CH\cdot NMe\cdot CO\cdot NH_2$, is obtained by the action of potassium cyanate on methyluramil, the latter being prepared by heating an aqueous solution of alloxan with methylamine sulphite for 3 hours at 70—75°, and saturating with hydrogen chloride the solution of methylamine methylthionurate thus produced; small quantities of uramil and ψ-uric acid occur as by-products in this change. The conversion of 7-methyl-ψ-uric acid into 7-methyluric acid is much more rapid than in the case of ψ-uric acid or the dimethyl derivative; a 1 per cent. solution of hydrochloric acid will bring about the change, which also proceeds slowly when an aqueous solution is heated at 100° in absence of acid. 3 : 7-Dimethyluric acid is conveniently prepared from 7-methyluric acid by heating the anhydrous lead derivative with ethereal methylic iodide for 12 hours at 170—175°; on dissolving the product in water, hydrogen sulphide liberates 3 : 7-dimethyluric acid from the solution.

1 : 3 : 7-*Trimethyluramil*,  $CO<\begin{array}{l}NMe\cdot CO\\NMe\cdot CO\end{array}>CH\cdot NHMe$, is prepared by heating dimethylalloxan with methylamine sulphite for 1 hour at 65—70°; when the two substances are mixed, a feeble, red coloration is developed, and after some time has elapsed, the solution deposits colourless, prismatic needles of the *additive compound*, $C_6N_2O_4H_6 + NH_2Me,H_2SO_3$. Trimethyluramil crystallises from water in colourless needles, and gradually decomposes when the aqueous solution is boiled;

the dry substance is, however, quite stable. It becomes red at 100°, and completely decomposes at about 200°.

1 : 3 : 7-*Trimethyl-ψ-uric acid*,  $CO<\begin{matrix}NMe\cdot CO\\NMe\cdot CO\end{matrix}>CH\cdot NMe\cdot CO\cdot NH_2$, obtained by treating trimethyluramil with an aqueous solution of potassium cyanate, crystallises from water in colourless prisms containing $1H_2O$, which is eliminated at 110°; when heated rapidly, it melts and decomposes at 195°, but if the temperature is slowly raised, decomposition occurs at 180—190°, the product remaining solid at 300°. Trimethyluramil is converted into hydroxycaffeine under the influence of a hot, 1 per cent. solution of hydrochloric acid, and when hydroxycaffeine is methylated, a mixture of methoxycaffeine and tetramethyluric acid is obtained; the latter substance melts at 223° (228° corrected), and not at 218°, as previously stated.

2-*Amido*-6 : 8-*dioxypurine*,



$$NH_2\cdot C\ll\begin{matrix}NH\cdot CO\cdot C\cdot NH\\ \quad\quad\quad\quad \| \\ N\text{———}C\cdot NH\end{matrix}>CO \text{ or } NH_2\cdot C\ll\begin{matrix}N\cdot CO\cdot C\cdot NH\\ \quad\quad\quad \| \\ NH\text{—}C\cdot NH\end{matrix}>CO,$$

is prepared from imido-ψ-uric acid (Traube, Abstr., 1894, i, 9) by the action of hydrochloric acid of sp. gr. = 1·19 in closed tubes at 120°; it dissolves with extreme difficulty in water, and decomposes without fusion at about 380°. The *sulphate*, and the *ammonium* derivative are decomposed on boiling their aqueous solutions; the *sodium* derivative forms colourless, microscopic needles, and the *barium* derivative dissolves with great difficulty in water. Hot nitric acid rapidly decomposes the substance, but the solution does not give the murexide reaction in a striking manner; chlorine converts amidodioxypurine into guanidine hydrochloride.

Amidodioxypurine is also produced when bromoguanine is treated with hydrochloric acid in sealed tubes at 130°. M. O. F.

Substituted Amides of Oxalic Acid. By WILHELM KERP and KARL UNGER (*Ber.*, 1897, **30**, 579—585).—Although amidoacetic acid has no action on ethylic cholate at the ordinary temperature, substituted amides of oxalic acid are readily obtained when the substance is brought into contact with ethylic oxalate, oxamethane, and ethylic oxamethaneacetate; ethylic amidoacetate also acts on the chloride of monethylic oxalate.

Oxalyldiglycocine (*oxamidediacetic acid*), $C_2O_2(NH\cdot CH_2\cdot COOH)_2$, is produced on adding ethylic oxalate (1 mol.) to an aqueous solution of potassium amidoacetate (2 mols.); it is somewhat soluble in boiling water, but dissolves sparingly in the cold agent, and is insoluble in common solvents. When rapidly heated, it melts and decomposes at 250°. The *silver* salt is colourless, and resists the action of light, and the *methylic* salt crystallises in lustrous, colourless leaflets, and melts at 138—140°. The *monethylic* salt is obtained by the action of potassium amidoacetate on ethylic oxamethaneacetate; it crystallises in slender, white needles, and melts at 164—165°.

Amido-oxalylglycocine (*oxamidoacetic acid*),

$$NH_2\cdot CO\cdot CO\cdot NH\cdot CH_2\cdot COOH,$$

is produced when potassium amidoacetate acts on oxamethane; it crystallises in colourless needles, becomes brown at 214°, and melts, and decomposes at 224—228°. The *potassium* salt contains $2H_2O$, and the *silver* salt is colourless, and resists the action of light.

Ethylic oxamethaneacetate, $COOEt{\cdot}CO{\cdot}NH{\cdot}CH_2{\cdot}COOEt$, is obtained by heating the chloride of monethylic oxalate with ethylic amidoacetate hydrochloride suspended in dry benzene in a reflux apparatus; it is a colourless, viscous liquid, having the sp. gr. = 1·183 at 20°, and boils at 197—198° under a pressure of 12 mm.

Ethylic oxamethanepropionate, $COOEt{\cdot}CO{\cdot}NH{\cdot}CHMe{\cdot}COOEt$, is produced when the chloride of monethylic oxalate is heated with the hydrochloride of ethylic amidopropionate suspended in dry benzene in a reflux apparatus; it boils at 169—172° under a pressure of 14 mm.

M. O. F.

Semioxamazide. By Wilhelm Kerp and Karl Unger (*Ber.*, 1897, **30**, 585—593).—The readiness with which semicarbazide combines with aldehydes and ketones, coupled with the disadvantage offered by the agent in frequently giving rise to two modifications of semicarbazone, has led the authors to prepare semioxamazide, and study its behaviour towards the groups in question; whilst, however, aldehydes produce in quantitative yield semioxamazones which melt at definite temperatures, the action of semioxamazide on ketones is less general, and usually proceeds under certain limiting conditions.

Semioxamazide, $NH_2{\cdot}CO{\cdot}CO{\cdot}NH{\cdot}NH_2$, is obtained by gently heating oxamethane with an alcoholic solution of hydrazine on the water bath; it crystallises in slender, lustrous leaflets, and melts and decomposes at 220—221°. The substance dissolves readily in hot water, and sparingly in the cold agent, being insoluble in alcohol and ether; acids and alkalis dissolve it readily, and a cold solution of silver nitrate is immediately reduced. The *hydrochloride* is precipitated in long, slender, colourless needles on adding alcohol to the aqueous solution, and the *sulphate*, prepared in a similar manner, also crystallises in white needles. When a concentrated solution of copper chloride (1 mol.) is added to semioxamazide hydrochloride dissolved in the minimum quantity of water, a deep blue, crystalline *copper chloride* derivative, $NH_2{\cdot}CO{\cdot}CO{\cdot}N(CuCl){\cdot}NH_2,HCl$, separates after a few days, associated with a green, pulverulent *copper* derivative, $(C_2O_2N_3H_4)_2Cu_2 + H_2O$. The *carbamide* crystallises from hot water in slender needles, and melts and decomposes at 215°. When semioxamazide is melted, or heated in sealed tubes for 2 hours at 145°, ammonia is liberated and two compounds are formed, one of which is a polymeride of cyanic acid; this substance probably has the constitution $\begin{matrix}CO{\cdot}NH\\ | \quad\ \ |\\ CO{\cdot}NH\end{matrix}$, and the compound associated with it is the ammonium derivative.

Benzaldehyde semioxamazone is a colourless, finely divided powder, almost insoluble in common solvents; it sublimes very readily in long threads, and melts at 264°, with slight evolution of gas.

Cinnamaldehyde semioxamazone is a white powder and sublimes in woolly needles; when rapidly heated, it melts and decomposes at 274°.

Salicylaldehyde semioxamazone crystallises from hot dilute alcohol in small, lustrous, pale yellow needles, and melts at 255°.

Citraldehyde semioxamazone is obtained as a white spongy mass, insoluble in water and ether, but dissolving readily in alcohol; it melts at 190—191°.

Furfuraldehyde semioxamazone is a yellowish-white powder which becomes brown at 240°, sinters at 259°, and melts, decomposing, at 264°; when heated cautiously, it sublimes in small, yellowish-white needles. The insoluble character of this substance recommends its application in the estimation of those carbohydrates which yield furfuraldehyde on hydrolysis; quantitative experiments carried out in this direction have invariably led to satisfactory results.

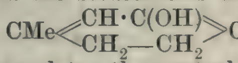
Acetophenone semioxamazone crystallises from alcohol in long, lustrous, white needles; it melts at 214°.

Ethylic acetoacetate semioxamazone separates from alcohol in slender needles and melts at 125—127°.

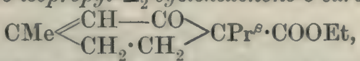
Carvone semioxamazone crystallises in aggregates of snow-white needles and melts at 187—188°.

Methylhexanone semioxamazone slowly separates from a mixture of alcohol and ether in white needles and melts at 153—154°.

Menthone semioxamazone crystallises from alcohol in aggregates of white needles and melts at 177°. M. O. F.

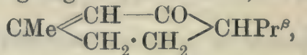
Hagemann's Ethylic Methylcyclohexenonecarboxylates, and their Conversion into an Isomeride of Camphor. By JOHANN ANTON CALLENBACH (*Ber.*, 1897, **30**, 639—646. Compare Abstr., 1893, i, 393).—By the action of methylenic iodide on ethylic sodioacetoacetate, Hagemann obtained a mixture of two isomeric substances having the composition $C_{10}H_{14}O_3$, separable by treatment with dilute caustic soda, the acidic modification developing a deep red coloration with ferric chloride, towards which the neutral form is indifferent; the constitutional difference between the two isomerides is not of the character described by Hagemann (*loc. cit.*), the substances being tautomeric, and the structure of the acidic form is represented by the expression  $\mathrm{CMe}<\begin{matrix}\mathrm{CH\cdot C(OH)}\\ \mathrm{CH_2—CH_2}\end{matrix}>\mathrm{C\cdot COOEt}$, the ketonic modification of which formulates the neutral salt. This is shown by the complete conversion of the ketonic into the enolic form under the influence of sodium ethoxide, and by the production of a single isopropyl derivative from both salts; moreover, the sp. gr. = 1·0816 in both cases, and the enolic form has the refractive index $n_D = 1·4859$, giving the molecular refraction 48·38, whilst the ketonic modification has the refractive index $n_D = 1·4823$, and the molecular refraction 47·95.

Ethylic-3-methyl-6-isopropyl-Δ_2-cyclohexenone-6-carboxylate,



$$\mathrm{CMe}<\begin{matrix}\mathrm{CH—CO}\\ \mathrm{CH_2\cdot CH_2}\end{matrix}>\mathrm{CPr^{\beta}\cdot COOEt},$$

is obtained by the action of sodium ethoxide and isopropylic iodide both on the ketonic and on the enolic salts; it boils at 157—158° under a pressure of 18 mm., has the sp. gr. = 1·0646 at 17°, and the refractive index $n_D = 1·4838$. *3-Methyl-6-isopropyl-Δ_2-cyclohexenonecarboxylic acid* crystallises from light petroleum, ether, or benzene in beautiful, transparent prisms melting at 119—120°, and dissolves readily in water; the *silver* salt crystallises from water in long, colourless, transparent needles, and resists the action of light.

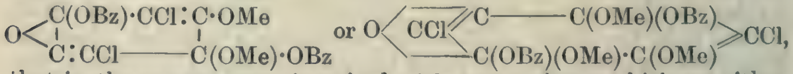
When the foregoing acid is distilled, carbonic anhydride is eliminated, and the *ketone*,  $CMe<\begin{matrix}CH—CO\\CH_2\cdot CH_2\end{matrix}>CHPr^{\beta}$, produced; this compound, a highly refractive oil having the odour of camphor, is isomeric with that substance, and boils at 217—219°. The *oxime* separates from light petroleum in beautiful, lustrous crystals belonging to the monoclinic system. M. O. F.

Effect of Light on the Displacement of Bromine and Iodine from Organic Bromides and Iodides. By J. H. KASTLE and W. A. BEATTY (*Amer. Chem. J.*, 1897, **19**, 139—149).—By the action of light on the dibromo-derivative of benzenesulphonamide, bromine is liberated even in the presence of water. From the dichloro-derivative of parabromobenzenesulphonamide, chlorine is first liberated, which then displaces bromine from the benzene ring.

From the results of numerous experiments with bromo- and iodo-compounds, the authors draw the following conclusions.

Bromine and iodine are displaced from their most stable organic compounds by means of chlorine water, and it seems probable that in presence of sunlight, chlorine "not only displaces but replaces bromine and iodine in their aromatic derivatives." A. W. C.

Oxide of Dichlorodimethoxyquinoldibenzoate. By C. LORING JACKSON and H. A. TORREY (*Ber.*, 1897, **30**, 527—531. Compare Abstr., 1896, i, 155).—The oxide, $C_6Cl_2(OMe)_2(OBz)_2O$, is now shown to have the constitution



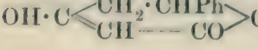
that is, the oxygen atom is united with two carbons, which are either in the ortho- or meta-position relatively to one another.

Amylamine reacts with the oxide, yielding a purple-red compound, $C_5H_{11}\cdot NH\cdot C_6Cl_2O_2\cdot NH_2(OH)\cdot C_5H_{11}$, which melts at 181—182°. The *silver* and *barium* salts and the free phenol, *dichloroamylaminohydroxyquinone*, $C_5H_{11}\cdot NH\cdot C_6Cl_2O_2\cdot OH$, which melts at 186—187°, are described.

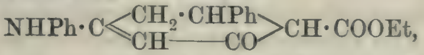
Sodium methoxide converts the oxide into the sodium salt of dichlorodimethoxyquinonedimethylhemiacetal. J. J. S.

Synthesis of Hydrogenised Derivatives of Resorcinol. By DANIEL VORLÄNDER (*Annalen*, 1897, **294**, 253—269).—The author discusses and summarises the results described in the following abstracts. M. O. F.

Synthesis and Hydrolysis of Dihydroresorcinol. By DANIEL VORLÄNDER (*Annalen*, 1897, **294**, 269—273. Compare Abstr., 1896, i, 20).—*Ethylic γ-acetylbutyrate* is a colourless liquid which boils at 221—222°; as already stated (*loc. cit.*), sodium ethoxide converts the salt into the sodium derivative of dihydroresorcinol. M. O. F.

Alkyldihydroresorcylic Acids. By DANIEL VORLÄNDER (*Annalen*, 1897, **294**, 273—301).—*Phenyldihydroresorcylic acid*,  $OH\cdot C\lessgtr\begin{matrix}CH_2\cdot CHPh\\CH—CO\end{matrix}>CH\cdot COOH$, is produced in the form of its methylic salt when methylic malonate acts on benzylideneacetone in methylic alcohol solution under the influence of sodium methoxide; it melts at about 100°, liberating carbonic anhydride, and giving rise to phenyldihydroresorcinol. The *methylic* salt crystallises from boiling water or very dilute methylic alcohol in needles, and melts at 162°; the ethylic salt has been already described (Abstr., 1894, i, 527). Owing to the presence of a free hydroxylic group, these derivatives are phenolic in character, and consequently give rise to ethers. The *methyl* ether of the methylic salt crystallises from dilute methylic alcohol in lustrous plates, and melts at 110—111°; the *ethyl* ether of the ethylic salt boils and partly decomposes at 250—260° under a pressure of 30 mm.

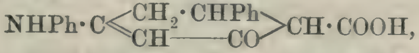
Ethylic anilidophenyldihydroresorcylate,



$$\mathrm{NHPh\cdot C}\Big\langle\begin{matrix}\mathrm{CH_2\cdot CHPh}\\ \mathrm{CH{-}{-}{-}CO}\end{matrix}\Big\rangle\mathrm{CH\cdot COOEt},$$

is obtained by heating ethylic phenyldihydroresorcylate with 4 parts of aniline during 8—10 hours, and crystallises from alcohol in large prisms melting at 144—145°; resembling the other alkylamides, this substance is neutral in character, resists the action of hydroxylamine and alcoholic ammonia, and develops a brown coloration with ferric chloride. The *paratoluidido*-compound crystallises in colourless needles and melts at 214°; the *ethyl* derivative melts at 70°. When the ethyltoluidido-compound is heated with 10 parts of fuming hydrochloric acid in sealed tubes at 100° during 4 hours, ethyltoluidine is eliminated; the other alkylamides exhibit analogous behaviour under the influence of hydrochloric acid. The *paraphenetidido*-compound separates from alcohol in concentric groups of crystals, and melts at 168°.

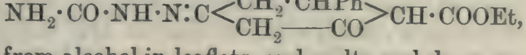
Anilidophenyldihydroresorcylic acid,



$$\mathrm{NHPh\cdot C}\Big\langle\begin{matrix}\mathrm{CH_2\cdot CHPh}\\ \mathrm{CH{-}{-}{-}CO}\end{matrix}\Big\rangle\mathrm{CH\cdot COOH},$$

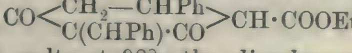
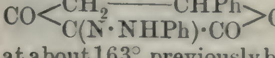
obtained by hydrolysing the ethylic salt with cold alcoholic potash, is a white powder which melts and evolves carbonic anhydride at about 190°, yielding *anilidophenyldihydroresorcinol*, which melts at 240°. *Toluidophenyldihydroresorcylic acid* yields *toluidophenyldihydroresorcinol* which melts at 215°; this substance is also produced when the attempt is made to crystallise the acid from hot glacial acetic acid.

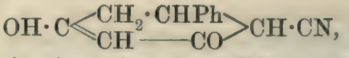
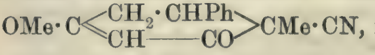
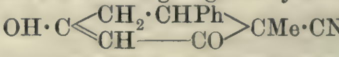
The *semicarbazone* of ethylic phenyldihydroresorcylate,



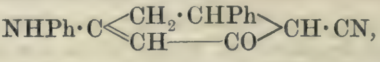
$$\mathrm{NH_2\cdot CO\cdot NH\cdot N\colon C}\Big\langle\begin{matrix}\mathrm{CH_2\cdot CHPh}\\ \mathrm{CH_2{-}{-}{-}CO}\end{matrix}\Big\rangle\mathrm{CH\cdot COOEt},$$

crystallises from alcohol in leaflets, and melts and decomposes at 208°. The phenylhydrazone melts at 130°, as stated by Knoevenagel, and not at 74—75°, as stated by Michael and Freer.

When ethylic phenyldihydroresorcylate is heated with benzaldehyde and acetic anhydride in sealed tubes at 150—160° during 8—10 hours, the *benzylidene* derivative,  $\mathrm{CO}\Big\langle\begin{matrix}\mathrm{CH_2{-}CHPh}\\ \mathrm{C(CHPh)\cdot CO}\end{matrix}\Big\rangle\mathrm{CH\cdot COOEt}$, is formed as a white substance which melts at 98°; the *diazobenzene* derivative,  $\mathrm{CO}\Big\langle\begin{matrix}\mathrm{CH_2{-}{-}{-}CHPh}\\ \mathrm{C(N\cdot NHPh)\cdot CO}\end{matrix}\Big\rangle\mathrm{CH\cdot COOEt}$, crystallises from alcohol, and melts at about 163°, previously becoming brown and undergoing decomposition.

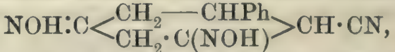
Phenyldihydroresorcylonitrile,  $OH\cdot C<\begin{array}{l}CH_2\cdot CHPh\\ CH\text{———}CO\end{array}>CH\cdot CN$, is obtained in the form of sodium derivative when benzylideneacetone is heated with ethylic cyanacetate and alcoholic sodium ethoxide, and melts at about 180°; when treated with boiling, dilute sulphuric acid, phenyldihydroresorcinol is formed. The *methyl* ether crystallises in leaflets and melts at 173°. The *dimethyl* derivative of the nitrile,  $OMe\cdot C<\begin{array}{l}CH_2\cdot CHPh\\ CH\text{———}CO\end{array}>CMe\cdot CN$, is obtained by the action of methylic alcohol and sodium methoxide on the foregoing methyl ether and melts at 136°; the *methyl-nitrile*,  $OH\cdot C<\begin{array}{l}CH_2\cdot CHPh\\ CH\text{———}CO\end{array}>CMe\cdot CN$, is produced on hydrolysing the dimethylnitrile with aqueous sodium carbonate, and melts at 174°. The *hydroxylamine* derivative of the methyl-nitrile, $C_{14}H_{17}O_3N_3$, melts and evolves gas at 155°.

Anilidophenyldihydroresorcylonitrile,

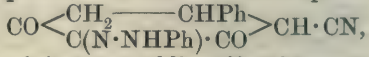


$$NHPh\cdot C<\begin{array}{l}CH_2\cdot CHPh\\ CH\text{———}CO\end{array}>CH\cdot CN,$$

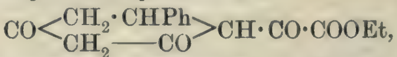
crystallises from alcohol and melts at 230°; the *dioxime*,



$$NOH{:}C<\begin{array}{l}CH_2\text{——}CHPh\\ CH_2\cdot C(NOH)\end{array}>CH\cdot CN,$$

crystallises from alcohol in colourless plates, and melts and decomposes at 182°. The *diazobenzene* derivative,  $CO<\begin{array}{l}CH_2\text{———}CHPh\\ C(N\cdot NHPh)\cdot CO\end{array}>CH\cdot CN$, is obtained as a yellow, crystalline precipitate on adding diazobenzene chloride to the nitrile dissolved in sodium carbonate; it melts at 110°, and becomes brownish-red after lapse of time.

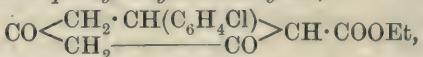
Ethylic phenyldihydroresorcyloxalate,



$$CO<\begin{array}{l}CH_2\cdot CHPh\\ CH_2\text{——}CO\end{array}>CH\cdot CO\cdot COOEt,$$

is obtained from benzylideneacetone and the sodium derivative of ethylic oxalacetate; it crystallises from alcohol in leaflets, and melts at 131°.

Ethylic orthochlorophenyldihydroresorcylate,

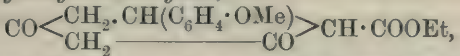


$$CO<\begin{array}{l}CH_2\cdot CH(C_6H_4Cl)\\ CH_2\text{————}CO\end{array}>CH\cdot COOEt,$$

is prepared from the sodium derivative of ethylic malonate and orthochlorobenzylideneacetone; it melts at 142°. *Orthochlorobenzylideneacetone* is obtained from orthochlorobenzaldehyde and acetone in presence of 10 per cent. caustic soda, and boils at 189° under a pressure of 30 mm.; the *oxime* crystallises from dilute alcohol in lustrous, white needles, and melts at 117°.

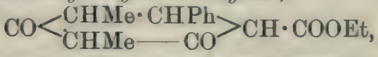
Ethylic paranitrophenyldihydroresorcylate, which is formed when paranitrobenzylideneacetone is heated with alcoholic sodium ethoxide and ethylic malonate on the water bath, crystallises from alcohol in small, colourless prisms containing 1 molecule of the solvent; this is removed at 110°, and it then melts at 140°. *Ethylic metanitrophenyldihydroresorcylate* separates from alcohol in small, white crystals, and melts at 163°. *Metanitrobenzylideneacetone* crystallises from glacial acetic acid in small prisms, and melts at 94—95°; the phenylhydrazone melts at 155°.

Ethylic anisyldihydroresorcylate,


$$\mathrm{CO}<\begin{array}{l}\mathrm{CH_2.CH(C_6H_4\cdot OMe)}\\ \mathrm{CH_2}\text{————————}\mathrm{CO}\end{array}>\mathrm{CH\cdot COOEt},$$

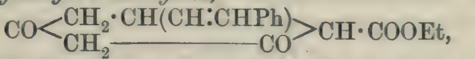
is obtained from anisylideneacetone and ethylic sodiomalonate, and also from ethylic paramethoxycinnamate and ethylic sodioacetoacetate; it crystallises from glacial acetic acid and melts at 160°. The *paraphenetidido*-derivative melts at 217°. *Ethylic paramethoxycinnamate* melts at 48—49°, and boils at 245° under a pressure of 120 mm.

Methylic phenyldimethyldihydroresorcylate,


$$\mathrm{CO}<\begin{array}{l}\mathrm{CHMe\cdot CHPh}\\ \mathrm{CHMe}\text{——}\mathrm{CO}\end{array}>\mathrm{CH\cdot COOEt},$$

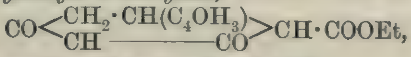
prepared from methylic sodiomalonate and benzylidenediethyl ketone, crystallises from methylic alcohol in small prisms melting at 185°; *phenyldimethyldihydroresorcylic acid* melts at about 100°, evolving carbonic anhydride, and yielding phenyldimethyldihydroresorcinol.

Ethylic styryldihydroresorcylate,

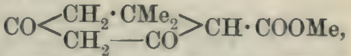

$$\mathrm{CO}<\begin{array}{l}\mathrm{CH_2\cdot CH(CH{:}CHPh)}\\ \mathrm{CH_2}\text{————————}\mathrm{CO}\end{array}>\mathrm{CH\cdot COOEt},$$

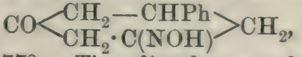
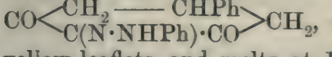
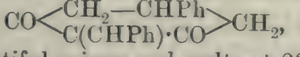
crystallises from dilute alcohol in leaflets, and melts at 138°.

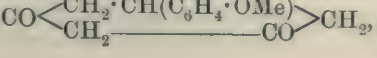
Ethylic furfuryldihydroresorcylate,

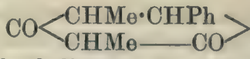

$$\mathrm{CO}<\begin{array}{l}\mathrm{CH_2\cdot CH(C_4OH_3)}\\ \mathrm{CH}\text{——————}\mathrm{CO}\end{array}>\mathrm{CH\cdot COOEt},$$

crystallises from acetic acid and melts at 102°.

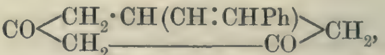
Methylic dimethyldihydroresorcylate,  $\mathrm{CO}<\begin{array}{l}\mathrm{CH_2\cdot CMe_2}\\ \mathrm{CH_2}\text{—}\mathrm{CO}\end{array}>\mathrm{CH\cdot COOMe}$, prepared from methylic malonate and mesitylic oxide, crystallises in long, slender needles melting at 102°; the aqueous solution develops a violet-brown coloration with ferric chloride. The *ethylic* salt melts at 75°, and forms a *sodium* derivative. The *paratoluidido*-derivative of the methylic salt melts at 147°. The *semicarbazone* of the ethylic salt crystallises in white scales and melts at 212°. M. O. F.

Alkyldihydroresorcinols. By DANIEL VORLÄNDER and JOH. ERIG (*Annalen*, 1897, **294**, 302—316).—Phenyldihydroresorcinol, obtained by crystallising phenyldihydroresorcylic acid from acetic acid, has been already described; the *sodium* derivative is crystalline, and the *lead* derivative a white precipitate. The *benzyl* ether crystallises from alcohol in small, lustrous leaflets, and melts at 129—130°. The ethyl ether and anilide have been already described by Stollé; the *ethylanilido-*, *paratoluidido-*, and *paraphenetidido*-derivatives melt at 135°, 215°, and 207° respectively. The *monoxime*,  $\mathrm{CO}<\begin{array}{l}\mathrm{CH_2}\text{—}\mathrm{CHPh}\\ \mathrm{CH_2\cdot C(NOH)}\end{array}>\mathrm{CH_2}$, melts at 79°—82°, and the *dioxime* at 177°. The *diazobenzene* derivative,  $\mathrm{CO}<\begin{array}{l}\mathrm{CH_2}\text{——}\mathrm{CHPh}\\ \mathrm{C(N\cdot NHPh)\cdot CO}\end{array}>\mathrm{CH_2}$, crystallises from alcohol in beautiful, yellow leaflets, and melts at 172°; it forms a *dioxime* which crystallises from benzene and melts and decomposes at 228°. The *benzylidene* derivative,  $\mathrm{CO}<\begin{array}{l}\mathrm{CH_2}\text{—}\mathrm{CHPh}\\ \mathrm{C(CHPh)\cdot CO}\end{array}>\mathrm{CH_2}$, crystallises from glacial acetic acid in beautiful prisms and melts at 232°.

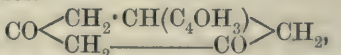
Anisyldihydrorescinol,  $\mathrm{CO}<\begin{array}{l}\mathrm{CH_2\cdot CH(C_6H_4\cdot OMe)}\\ \mathrm{CH_2}\text{————————}\mathrm{CO}\end{array}>\mathrm{CH_2}$, crystallises from alcohol in slender needles, and melts at about 185°; the *paraphenetidido*-derivative crystallises in small, white leaflets, melting at 226°, and the *dioxime* melts at 182—184°.



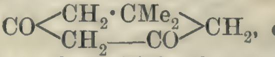
Phenyldimethyldihydroresorcinol, $CO<\begin{matrix}CHMe\cdot CHPh\\ CHMe\text{——}CO\end{matrix}>CH_2$, melts at about 175°, and yields a yellow oil of disagreeable odour after some time.



Styryldihydroresorcinol, $CO<\begin{matrix}CH_2\cdot CH(CH{:}CHPh)\\ CH_2\text{————}CO\end{matrix}>CH_2$, crystallises from alcohol or dilute acetic acid in white needles and melts at about 188°, when it decomposes.



Furfuryldihydroresorcinol, $CO<\begin{matrix}CH_2\cdot CH(C_4OH_3)\\ CH_2\text{————}CO\end{matrix}>CH_2$, crystallises from hot water in prisms, and melts and decomposes at about 150°; the *anilido*-derivative crystallises from alcohol in small prisms and melts at 214°, the *dioxime* sinters at 175° and melts at about 180°, and the *diazobenzene* derivative at 152°.



Dimethyldihydroresorcinol, $CO<\begin{matrix}CH_2\cdot CMe_2\\ CH_2\text{——}CO\end{matrix}>CH_2$, crystallises from hot water in plates, and melts at about 150°; the *paratoluidido*-derivative melts at 200°, and the *dioxime* at 176°. *Methylenebisdimethyldihydroresorcinol* crystallises from alcohol in needles, and melts at 189°.

M. O. F.

Constitution of Bromophenacetin. By O. HODUREK (*Ber.*, 1897, 30, 477—480).—*Acetobromophenetidine* (*bromophenacetin*),

$OEt\cdot C_6H_3Br\cdot NHAc, [OEt : Br : NHAc = 1 : 2 : 4]$,

obtained by the action of sodium hypobromite and hydrochloric acid on acetophenetidine dissolved in acetic acid, melts at 107°. When heated with concentrated hydrochloric acid, it is converted into *orthobromoparaphenetidine hydrochloride*, $OEt\cdot C_6H_3Br\cdot NH_2,HCl$, which is insoluble in hydrochloric acid; the free *base* melts at 46°, boils at 189° (pressure = 20 mm.), and has powerful reducing properties. The *sulphate* is a white, crystalline salt, readily soluble in water; the *mercurochloride* is only sparingly soluble. When the base is diazotised in alcoholic solution, it is converted into orthobromophenetoil, and this, on being heated with hydrochloric acid at 180—190°, yields orthobromophenol. The constitution of the original bromophenacetin is thus proved. *Diacetorthobromoparaphenetidide* is obtained when bromophenacetin is heated with acetic anhydride; it is a white, amorphous powder which melts at 90°.

When heated with hydriodic acid, bromophenacetin yields *orthobromoparamidophenol hydriodide*, which crystallises in yellow plates and has a powerful reducing action. The *hydrochloride* is extremely unstable.

A. H.

Phenacyl Compounds. By FRANZ KUNCKELL (*Ber.*, 1897, 30, 573—577. Compare Bischler, Abstr., 1892, 1465).—*Phenacylmetabromaniline*, $COPh\cdot CH_2\cdot NH\cdot C_6H_4Br$, is produced on mixing bromacetophenone with metabromaniline (2 mols.), and melts at 137°; the *hydrochloride* forms nacreous leaflets, and melts at 163°. *Phenacylparachloraniline* crystallises from a mixture of chloroform and alcohol, and melts at 167°. *Metanitrophenacylparachloraniline* crystallises in yellow needles, and melts at 197°; it is isomeric with the *nitrophenacylparachloraniline* obtained by nitrating phenacylparachloraniline, which crystallises in reddish-yellow needles, and melts at 181°.

*Phenacyl-*as*-metaxylidine*, $COPh{\cdot}CH_2{\cdot}NH{\cdot}C_6H_3Me_2$, forms yellow needles, and melts at 98°; the *hydrochloride* is colourless, and melts at 147°. *Metanitrophenacyl-*as*-metaxylidine* crystallises from alcohol in dark-red needles and melts at 153°.

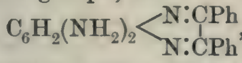
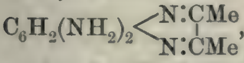
Phenacyl-α-naphthylamine and *phenacyl-β-naphthylamine* melt at 125° and 150° respectively. *Metanitrophenacyl-β-naphthylamine* crystallises in golden-yellow leaflets, and melts at 179°.

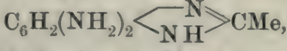
1-*Phenacyltetrahydroquinoline*, $COPh{\cdot}CH_2{\cdot}NC_9H_{10}$, crystallises from alcohol in yellow needles and melts at 104°; 1-*metanitrophenacyltetrahydroquinoline* forms golden-yellow leaflets and melts at 145°.

Phenacylparaphenetidine, $COPh{\cdot}CH_2{\cdot}NH{\cdot}C_6H_4{\cdot}OEt$, crystallises from alcohol in long, yellow needles and melts at 102°.

Benzoylmethyl paracresyl ether, $COPh{\cdot}CH_2{\cdot}O{\cdot}C_6H_4Me$, obtained by heating paracresol with bromacetophenone and alcoholic potash (compare Abstr., 1896, i, 151), melts at 68°. *Benzoylmethyl metatolyl ether* crystallises from alcohol in long needles and melts at 84°.

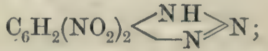
M. O. F.

Reduction of Picramide: Unsymmetrical Tetramidobenzene. By RUDOLF NIETZKI and HANS HAGENBACH (*Ber.*, 1897, **30**, 539—545).—Although repeated attempts have been made to reduce picramide to the corresponding unsymmetrical tetramidobenzene, none have hitherto met with success, owing mainly to the inefficiency of the reducing agent. It is now found, however, that if finely powdered picramide is gradually added to a mixture of stannous chloride, tin, and hydrochloric acid, the yellow colour of the amide rapidly disappears, and colourless needles of the tri-acid hydrochloride of as-*tetramidobenzene*, $C_6H_2(NH_2)_4,3HCl + H_2O$, make their appearance. On dissolving this hydrochloride in water and adding alcohol, a *di-acid* hydrochloride free from water can be obtained, whilst on decomposing a solution of this with sulphuric acid and adding alcohol, a di-acid sulphate separates in hexagonal leaflets. Tetramidobenzene combines with diketones, forming primary quinoxalines, which still contain two free amido-groups; thus with benzil, 1 : 3-*diamido*-2′ : 3′-*diphenylquinoxaline*,  $C_6H_2(NH_2)_2{<}\begin{matrix}N{:}CPh\\ |\\ N{:}CPh\end{matrix}$, is obtained in yellow leaflets melting at 260°; whilst with diacetyl, 1 : 3-*diamido*-2′ : 3′-*dimethylquinoxaline*,  $C_6H_2(NH_2)_2{<}\begin{matrix}N{:}CMe\\ |\\ N{:}CMe\end{matrix}$, a pale yellow substance melting at 228° is produced. The latter forms a hydrochloride which crystallises in dark red needles.

With sodium acetate and acetic anhydride, tetramidobenzene yields a *tetracetyl* derivative, crystallising from water or from glacial acetic acid in colourless needles melting at 245°. On heating this with dilute sulphuric acid, three acetyl residues are eliminated, an *acetanhydro*-base of the constitution  $C_6H_2(NH_2)_2{<}\begin{matrix}N\\ NH\end{matrix}{>}CMe$, being formed.

On oxidation with ferric chloride, tetramidobenzene is converted into the hydrochloride of a *diamidoquinoneimide*, which, since it is identical with the oxidation product derived from ordinary triamidophenol, must have the constitution $[O:(NH_2)_2:NH = 1:2:6:4]$.

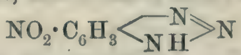
On partially reducing picramide with dilute ammonium sulphide, Norton and Elliott's *dinitrodiamidobenzene*, $[(NO_2)_2:(NH_2)_2 = 1:5:2:3]$, melting at 215°, is produced. The ortho-position of the amido-groups in this compound follows from the ready formation of an *acetanhydro*-compound, $C_6H_2(NO_2)_2{<}\genfrac{}{}{0pt}{}{N}{NH}{>}CMe$, and an *azimide*,



$$C_6H_2(NO_2)_2{<}\genfrac{}{}{0pt}{}{NH}{N}{>}N;$$

the former, which is produced on hydrolysing the acetyl derivative of the base with dilute sulphuric acid, crystallises in yellow needles melting at 242°, whilst the latter, formed by the action of nitrous acid on the hydrochloride, is obtained in colourless needles melting at 198°.

A *nitrotriamidobenzene* crystallising from alcohol in red scales which decompose at 260° without melting is produced when picramide is reduced with concentrated ammonium sulphide; it yields a *triacetyl* derivative melting at 243°, and a red, crystalline *acetanhydro*-base, $NH_2\cdot C_6H_2(NO_2){<}\genfrac{}{}{0pt}{}{N}{NH}{>}CMe_2$, with diacetyl, the nitrotriamidobenzene yields a feebly basic quinoxaline, and on acetylation with glacial acetic acid and a little acetic anhydride, a monacetyl derivative; this, on treatment with nitrous acid, yields an azimide by means of which the constitution of the compound can be deduced, since on hydrolysing the acetyl derivative, the *nitramidoazimide*, $NO_2\cdot C_6H_2(NH_2){<}\genfrac{}{}{0pt}{}{N}{NH}{>}N$, a dark yellow, infusible compound is produced, which on elimination of the amido-group by the ordinary method, yields a nitroazimide melting at 209°, and identical with the compound obtained by Hofmann from dinitraniline, and without doubt having the formula



$$NO_2\cdot C_6H_3{<}\genfrac{}{}{0pt}{}{N}{NH}{>}N \quad [N:NH:NO_2 = 2:3:5].$$

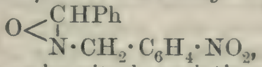
The position of the groups in the nitrotriamidobenzene must, therefore, be $[(NH_2)_3:NO_2 = 1:2:3:5]$. J. F. T.

Behaviour of Isomeric Diazotates towards Benzoic Chloride. By ARTHUR R. HANTZSCH (*Ber.*, 1897, **30**, 621—626).—The author finds, contrary to Bamberger's statement (this vol., i, 217), that both iso- and normal diazobenzenepotassium yield the same amount of nitrosobenzanilide when treated with benzoic chloride, and this takes place when a large excess of alkali and of benzoic chloride are present, and also when the theoretical amount of the chloride is used and only a slight excess of alkali, the normal and iso-compounds yielding the same amount of nitroso-compound. The parabromodiazotates behave in a similar manner. A. H.

Dynamical Researches on the Formation of Azo-dyes. By HEINRICH GOLDSCHMIDT and AUGUST MERZ (*Ber.*, 1897, **30**, 670—687).—The authors have quantitatively followed the formation of methylorange when an aqueous solution of dimethylaniline hydrochloride is added to an aqueous solution of paradiazobenzenesulphonic acid. They accomplished this by estimating the amount of unaltered diazobenzenesulphonic acid remaining in solution at the end of given intervals of time, which was effected by boiling with water, and measuring the amount of nitrogen liberated. The conclusions arrived at are: 1. In the combination of the hydrochloride of a primary amine with diazobenzenesulphonic acid, it is the base, liberated from the hydrochloride by hydrolysis, which acts with the sulphonic acid as such. 2. An excess of hydrochloric acid retards the formation of the dye. 3. The concentration of the hydrochloride and of the sulphonic acid has no influence on the reaction. Experiments have also been made in order to determine the velocity of formation of methyl-orange from diazobenzenesulphonic acid and dimethylaniline in acetic acid solution. In this case, the dye is formed much more quickly than with hydrochloric acid, and the amount of acetic acid present has but little influence on the velocity of formation.

The reaction between metacresol and paradiazobenzenesulphonic acid, both in alkaline solution, has also been studied quantitatively. The results arrived at are: 1. In the formation of hydroxyazo-dyes from phenols and diazo-salts in alkaline solution, the active agents are the free phenol liberated by the hydrolytic action of the water on the alkali salt and the *syn*-diazo-compound. 2. An excess of alkali retards the formation of the dye. 3. The time required for the reaction to take place varies directly with the concentration. Experiments with other phenols are being carried out. J. J. S.

β-Orthonitrobenzylhydroxylamine. By Carl Kjellin and K. G. Kuylenstjerna (*Ber.*, 1897, **30**, 517—518. Compare Paal and Poller, this vol., i, 184).—*β-Orthonitrobenzylisobenzaldoxime*,



$$O<\begin{matrix}CHPh\\ |\\ N\cdot CH_2\cdot C_6H_4\cdot NO_2,\end{matrix}$$

obtained in the usual way by nitrobenzylating *syn*-benzaldoxime, crystallises in colourless needles and melts at 104—105°. It is readily soluble in alcohol and benzene, but only sparingly in light petroleum. When boiled for 10 minutes with sufficient hydrochloric acid (20 per cent.) to dissolve it when hot, it is readily decomposed into *β-orthonitrobenzylhydroxylamine*, $NO_2\cdot C_6H_4\cdot CH_2\cdot NH\cdot OH$, the *hydrochloride* of which separates on cooling. The latter crystallises in colourless needles, melts at 185°, and decomposes at 190°; it is only sparingly soluble in cold hydrochloric acid, readily, however, in alcohol and water; it also readily reduces Fehling's solution. The *free base* crystallises in silky needles, melts at 70°, and at 140° turns dark blue; when kept for some time, the base turns brown.

Phenylorthonitrobenzylhydroxycarbamide,

$$NO_2\cdot C_6H_4\cdot CH_2\cdot N(OH)\cdot CO\cdot NHPh$$

(m. p. 141°), is readily formed by the action of phenylcarbimide on a benzene solution of the base. J. J. S.

Constitution of Benzanilide. By N. Knight (*Amer. Chem. J.*, 1897, **19**, 152—155).—By the action of benzoic chloride on benzenesulphonanilide or of benzenesulphonic chloride on benzanilide, dibenzoylanilide melting at 151° is produced. In both experiments, a beautiful, white, crystalline substance melting at 231° was obtained, which proved to be the aniline salt of benzenesulphonic acid.

Other bye-products are formed, but in quantities insufficient for satisfactory examination. The most definite of these is a substance crystallising in plates and melting at 212°. A. W. C.

Action of Acid Chlorides on the Imido-ethers and Isoanilides: Structure of the Silver Salts of the Anilides.

By Henry L. Wheeler and Percy T. Walden (*Amer. Chem. J.*, 1897, 19, 129—139).—Substituted imido-ethers or isoanilides react with acid chlorides, as in the following example, $CH_3{\cdot}O{\cdot}CH{:}NPh + Ph{\cdot}COCl = CH_3{\cdot}O{\cdot}CHCl{\cdot}NPh{\cdot}COPh$. This additive product then looses the elements of methylic chloride, yielding a mixed diacid anilide,

$$O{:}CH{\cdot}NPh{\cdot}COPh.$$

These mixed diacid anilides are decomposed by alkalis, giving a monacid anilide of the higher acid group. The explanation of the ease with which this reaction takes place is the existence of a double linking between the carbon and nitrogen. That this action is not a double decomposition or replacement of the alkyl group by the acid radicle, is shown by the fact that non-substituted imido-ethers react with acid chlorides with elimination of hydrogen chloride instead of alkyl chloride.

The action of acid chlorides on the silver salts of the anilides is analogous to the above, addition first taking place with subsequent removal of silver chloride, proving that in these silver salts the silver is joined to oxygen.

Non-substituted imido-ethers react with acid chlorides as stated above, the eliminated hydrogen chloride combining with excess of the imido-ether; when the product of the action is treated with acid or exposed to air, it takes up a molecule of water, and then decomposes into a diacid amide, showing that the latter, like the diacid anilides, have both acid groups attached to a nitrogen atom. This decomposition is also analogous to the action of acids on the silver salts of amides or anilides.

Halogens react with imido-ethers, one molecule of the former with two of the latter, giving halogen imido-ethers and the halogen hydride salt of the imido-ether.

Formoacetanilide, $COH{\cdot}NAcPh$, is obtained by the action of acetic chloride on phenylformimidoethyl ether. It crystallises from a mixture of ether and light petroleum in beautiful, brittle crystals melting at 56—57°. Sodium hydroxide converts it into acetanilide.

Formobenzanilide, $COH{\cdot}NBzPh$, produced from benzoic chloride and phenylformimidoethyl ether, is a solid crystallising in needles and melting at 112°. By the action of sodium hydroxide, it is converted into benzanilide.

Formobenzenesulphonanilide, $COH{\cdot}NPh{\cdot}SO_2Ph$, obtained from the imido-ether and benzenesulphonic chloride, crystallises in colourless, radiating needles melting at 148—149°; on boiling it with sodium hydroxide, benzenesulphonanilide is produced.

Formobenzorthotoluidide and *formobenzoparatoluidide*,

$$COH{\cdot}NBz{\cdot}C_6H_4Me,$$

are produced when benzoic chloride acts on ortho- or para-tolylformimidoethyl ether respectively. The former melts at 91°, the latter at 102°. On treatment with alkali, the corresponding benzotoluides are obtained.

Benzoylbenzimidoethylic ether, $OEt\cdot CPh\colon NBz$, formed when benzoic chloride acts on benzimidoethyl ether, melts at 65°. Alkalis are without action on this substance; but acids readily convert it into dibenzamide.

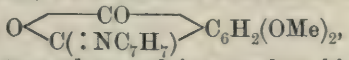
Acetobenzimidomethylic ether, $OMe\cdot CPh\colon NAc$, the product of the action of acetic chloride on benzimidomethyl ether, is a liquid boiling at 139° under a pressure of 15 mm. Dilute sulphuric acid converts it into acetobenzamide, which melts at 120°. The corresponding *acetobenzimidoethylic ether* is a liquid which distils at 151° under a pressure of 17 mm.

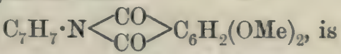
Benzobromimidomethylic ether and *benzoiodo-imidomethylic ether* are oily compounds obtained by the direct action of the halogen on benzimidomethyl ether.

A. W. C.

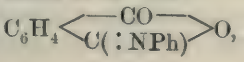
Isoimides. By P. HOJONIDES VAN DER MEULEN (*Rec. Trav. Chim.*, 1896, **15**, 282—287. Compare Hoogewerff and van Dorp, Abstr., 1896, i, 314).—*a-Hemipinobenzylamic acid*,

$$COOH\cdot C_6H_2(OMe)_2\cdot CO\cdot NH\cdot C_7H_7, [=1:3:4:2],$$

which is readily formed on gently warming hemipinic anhydride with an aqueous solution of benzylamine, is conveniently purified by precipitating it from its solution in hydrochloric acid and recrystallising the product from alcohol. It melts at 171—172°, is insoluble in ether, sparingly soluble in water, but readily so in acetone and chloroform. When the alcoholic mother liquor from the α-acid is diluted with water, it yields a small amount of the isomeric β-acid. α-Hemipinobenzylamic acid, when treated with acetic chloride, yields *a-hemipinobenzylisoimide*,  $O<\begin{matrix}CO\\C(:NC_7H_7)\end{matrix}>C_6H_2(OMe)_2$, the mixture is heated at 60° for 7 minutes and poured into carbon bisulphide, when the *hydrochloride* of the isoimide separates as an oil which quickly solidifies; it is collected, added to dry ether, and decomposed with a slight excess of aqueous potash (30 per cent.), care being taken to keep the mixture cold. The isoimide is obtained from its ethereal solution in fine needles which melt at 99—100°. It is necessary to expedite the above reactions, as the compound is readily decomposed by water, yielding hemipinobenzylamic acid.

Hempinobenzylimide,  $C_7H_7\cdot N<\begin{matrix}CO\\CO\end{matrix}>C_6H_2(OMe)_2$, is readily obtained by heating α-hemipinobenzylamic acid until the water which is produced just disappears. It crystallises in needles, melts at 128—132°, is readily soluble in chloroform and acetone, sparingly in water, and insoluble in ether.

β-Hemipinobenzylamic acid, $COOH\cdot C_6H_2(OMe)_2\cdot CO\cdot NH\cdot C_7H_7$ [= 2 : 3 : 4 : 1] is obtained when hemipinobenzylimide is warmed with caustic soda (5 per cent.) on the water bath. It melts at 161—162° and as regards its solubility resembles the α-acid. The *β-isoimide* crystallises in glistening plates and melts at 80—82°.

Phthalophenylisoimide  $C_6H_4<\begin{matrix}CO\\C(:NPh)\end{matrix}>O$, crystallises in small needles, melts at 115—117°, and is slowly transformed into the imide when heated at 250°. J. J. S.

Halogenised Ketones. By Franz Kunckell (*Ber.*, 1897, 30, 577—579).—*Paratolyl bromomethyl ketone*, $CH_2Br\cdot CO\cdot C_6H_4Me$, is obtained by adding bromine to a solution of the original ketone in glacial acetic acid, and after an interval of 12 hours, heating the liquid on the water bath; it crystallises from alcohol in colourless leaflets, and melts at 48—50°.

Paratolyl chloromethyl ketone, $CH_2Cl\cdot CO\cdot C_6H_4Me$, is prepared by the action of chloracetic chloride on toluene in presence of aluminium chloride; it crystallises in long needles and melts at 67°. *Metaxylyl chloromethyl ketone* and *paraxylyl chloromethyl ketone* melt at 62—63° and 32° respectively. *Pentethylphenyl chloromethyl ketone*,

$$CH_2Cl\cdot CO\cdot C_6Et_5,$$

forms short, white needles and melts at 104°. M. O. F.

Formation of Benzoic and Propionic Peroxides by Active Oxygen. By W. P. Jorissen (*Zeit. physikal. Chem.*, 1897, 22, 54—59).—The author has previously shown that, during the slow oxidation of benzaldehyde by oxygen, an equal portion of the gas is rendered 'active.' If acetic anhydride is mixed with the benzaldehyde and the surface increased by the addition of sand, the volume of oxygen absorbed is double that necessary for oxidation to benzoic acid. A similar result was obtained when the sand was omitted, in both cases benzoic peroxide was obtained from the residue, but in the absence of acetic anhydride, benzoic acid alone was produced. The author considers the results are to be expressed by the equations:

$$C_6H_5\cdot COH + O_2 = C_6H_5\cdot COOH + O\text{ (active)}$$
$$(CH_3\cdot CO)_2 + O\text{(active)} = (CH_3\cdot CO)_2O_2$$
$$(CH_3\cdot CO)_2O_2 + 2C_6H_5\cdot COH + O_2 = (C_6H_5\cdot CO)_2O_2 + 2\,CH_3\cdot COOH.$$

Similar experiments with propaldehyde and acetic anhydride gave similar results, but the ratio of oxygen absorbed to that absorbed in the absence of the anhydride was 1·75 : 1. The author explains this departure from the previous value of 2 : 1 to the fact that the vapour pressure of the aldehyde is much greater than that of the anhydride, and hence that the "active" oxygen does not find sufficient anhydride in its vicinity, when formed. L. M. J.

Pseudophenylacetic Acid. By Eduard Buchner (*Ber.*, 1897, 30, 632—636. Compare Abstr., 1896, i, 230).—*Isophenylacetic acid*, $C_7H_7\cdot COOH$, is the name applied by the author to the unsaturated acid obtained on hydrolysing ψ-phenylacetamide with aqueous soda; it crystallises from much boiling water in flat needles and melts at 71°. Although the substance decolorises a cold solution of potassium permanganate immediately, it is quite distinct from pseudophenylacetic acid, because it undergoes no change when exposed to air, and develops a yellow coloration when dissolved in concentrated sulphuric acid. A solution of ethylic ψ-phenylacetate in concentrated sulphuric acid is initially cherry-red, rapidly becoming violet, and finally blue, exhibiting moderately strong fluorescence; the absorption spectrum is very characteristic, and it is noteworthy that dihydrobenzene, when dissolved in alcoholic sulphuric acid, develops an intense blue coloration (Von

Baeyer, Abstr., 1892, 1075). The *barium* and *calcium* salts of isophenylacetic acid are readily soluble, but crystallise from highly concentrated solutions; the *silver* salt is very sensitive to light, and yields a crystalline distillate when heated. The *amide* crystallises from much boiling ether in flat, yellowish needles, and melts at 129°; hydrolysis with aqueous soda regenerates the acid. Isophenylacetic acid *monohydrobromide*, $C_7H_8Br\cdot COOH$, is obtained from the acid and glacial acetic acid saturated with hydrogen bromide at 0° (4 parts); it crystallises from a mixture of ether and petroleum, melts and evolves gas at 127°, and the solution in excess of sodium carbonate immediately decolorises potassium permanganate. The *dihydrobromide*, $C_7H_9Br_2\cdot COOH$, prepared by using 8 parts of the saturated solution of hydrogen bromide, crystallises from ether and melts at 164°, evolving a small quantity of gas; boiling water decomposes the substance, which undergoes no change in air, and alkaline potassium permanganate is at once reduced. When the dihydrobromide is reduced with sodium amalgam, an unsaturated, oily *tetrahydroisophenylacetic acid* is produced, further reduction giving rise to a mixture of substances; one of these is a saturated *acid*, $C_6H_{10}O_2$, which crystallises in needles, melts at 124—126°, and is volatile in an atmosphere of steam. The main product of ultimate reduction, however, is *hexahydroisophenylacetic acid*, a saturated oil, having an intensely disagreeable odour; the *amide* melts indefinitely at 184—186°. M. O. F.

Paranitrophenoxyacetic and Paramidophenoxyacetic Acids, and some of their Derivatives. By C. KYM (*J. pr. Chem.*, 1897, [ii], **55**, 113—123).—Paranitrophenoxyacetic acid is most conveniently prepared by hydrolysis of the ethylic salt, which is itself produced almost quantitatively when ethylic chloracetate is heated at 180° with sodium nitrophenol. The ethylic salt crystallises in pale yellow, lustrous needles, and melts at 75—76°. *Paranitrophenoxyacetanilide*, $NO_2\cdot C_6H_4\cdot O\cdot CH_2\cdot CO\cdot NHPh$, crystallises in pale, yellow, lustrous needles melting at 170—171°. *Paramidophenoxyacetanilide*, prepared by reducing the nitro-derivative with tin and hydrochloric acid, crystallises in long, colourless needles melting at 104—105°; *paracetamidophenoxyacetanilide* crystallises in lustrous, white plates, melting at 204—205°. *Paramidophenoxyacetic acid*, $NH_2\cdot C_6H_4\cdot O\cdot CH_2\cdot COOH$, which Fritsche (Abstr., 1880, 319) was unable to obtain, can be prepared by reducing the nitro-acid with tin and hydrochloric acid; it crystallises with $1H_2O$ in compact, white needles or prisms, and does not melt below 312°. The *ammonium* salt crystallises in slender needles, melting at 201—202°; the *hydrochloride* is a white, crystalline mass, which is soluble in alcohol. The *benzoyl*-derivative crystallises in fascicular groups of needles melting at 194—195°; and the *acetyl*-derivative in long, lustrous needles melting at 175—176°. It possesses antipyretic properties, but not to the same extent as phenacetin, which it resembles in constitution. Orthonitrophenol behaves towards ethylic chloracetate in a similar manner to the para-compound. The derivatives thus obtained have already been described. A. H.

Paramidophenoxyacetic Acid. By CURTIS C. HOWARD (*Ber.*, 1897, **30**, 545—548).—*Paramidophenoxyacetic acid*, $NH_2\cdot C_6H_4\cdot O\cdot CH_2\cdot COOH$, can be prepared either by the reduction of Fritzsche's paranitroparaphenoxyacetic acid, by means of tin and acetic acid, and hydrolysing the acetyl compound thus produced, or by the action of the sodium salt of paracetamidophenol on sodium monochloracetate. It separates from boiling water, in which it is only sparingly soluble, in prismatic crystals containing $1H_2O$; this it looses at 100°, and then does not melt at 300°. The *acetyl* derivative crystallises in slender needles with $1H_2O$, which it loses at 100°, and melts when anhydrous at 174°.

Uramidophenoxyacetic acid, $NH_2\cdot CO\cdot NH_2\cdot C_6H_4\cdot O\cdot CH_2\cdot COOH$, prepared from the amido-acid in the usual way, has a slightly acid taste; it crystallises from hot water in flat prisms melting at 195°, and containing $2H_2O$. The *ethylic* salt forms white, anhydrous needles melting at 148°.

The *hydrazine* of *paraphenoxyacetic acid*,

$$NH_2\cdot NH\cdot C_6H_4\cdot O\cdot CH_2\cdot COOH,$$

prepared by V. Meyer and Lecco's method, separates from its aqueous solution, on the addition of alcohol, in small, white crystals containing $1H_2O$, melts at 146°, and becomes yellow on exposure to the air.

J. F. T.

Tautomerism of Orthoaldehydic Acids, III. By CARL T. LIEBERMANN (*Ber.*, 1897, **30**, 691—697. Compare Abstr., 1896, i, 232 and 682).—In the present communication, it is shown that methylnoropianic acid reacts with aromatic bases in exactly the same way as opianic acid, the compounds produced having the oxyphthalide structure; they are, however, soluble in soda, since they contain phenolic hydroxyl groups.

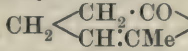
ψ-Ethylic methylnoropianate, $\begin{array}{l} O\text{—}CH\cdot OEt \\ \;| \qquad | \\ CO\cdot C_6H_2(OMe)\cdot OH \end{array}$, is obtained by boiling methylnoropianic acid for half an hour with ethylic alcohol; on adding light petroleum to its benzene solution, it separates in colourless needles melting at 104—106°. It is readily soluble in dilute soda, yielding the sodium derivative, which, however, is only sparingly soluble in concentrated soda solution; the acid is readily recovered from this pseudo-salt by boiling it with water.

ψ-Methylic methylnoropianate melts at 67—71°.

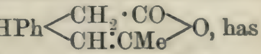
n-Ethylic methylnoropianate, $OMe\cdot C_6H_2(OH)(CHO)\cdot COOEt$, is formed when silver methylnoropianate is boiled for several hours with ethylic iodide; it melts at 102—103°, is sparingly soluble in benzene and in hot water, and differs from the ψ-ethylic salt in not being hydrolysed by boiling water.

An aqueous solution of mucobromic acid (1 mol.), on treatment with aniline ($\frac{3}{4}$ mol.), yields the anilide of mucobromic acid, but with excess of aniline (2 mols.), Hill and Palmer's mucohydroxybromic acid anilide, $OH\cdot C_4HBr(NPh)\cdot COOH$, is formed (Abstr., 1888, 451). Graebe and Bossel's benzaldehydedicarboxylic acid (*Annalen*, **290**, 215) reacts with α-naphthylamine to form an *α-naphthylamide*, $C_{10}H_8\cdot N\colon CH\cdot C_6H_3(COOH)_2$ melting at 202—207°. That the naphthylamide has the above constitution, and not that of an oxyphthalide, was proved by the analyses of its *barium* and *silver* derivatives.

The author recommends the formation of this α-naphthylamide as a ready means of purifying Graebe and Bossel's acid, the melting point of which is given as 162—165°, and not 175—178°. J. J. S.

δ-Ketonic Acids. By DANIEL VORLÄNDER and ARTHUR KNÖTZSCH (*Annalen*, 1897, **294**, 317—336).—*Ethylic α-acetylglutarate* is obtained by the action of ethylic acetoacetate on ethylic acrylate under the influence of sodium ethoxide, and boils at 174—177° under a pressure of 30 mm.; hydrolysis with cold alcoholic potash gives rise to glutaric acid, whilst boiling hydrochloric acid resolves the substance into carbonic anhydride and γ-acetylbutyric acid. The *oxime* of γ-acetylbutyric acid crystallises from water or benzene, and melts at 103—104°; the *lactone*,  $CH_2<\begin{matrix}CH_2\cdot CO\\ CH:CMe\end{matrix}>O$, is a colourless liquid which boils at 194—195°, and the *amide* and *paratoluidide* melt at 114° and 123° respectively.

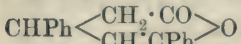
Acetonylbenzylmalonic acid, $COMe\cdot CH_2\cdot CHPh\cdot CH(COOH)_2$, is produced on treating ethylic phenyldihydroresorcylate with a boiling solution of barium hydroxide during 6—8 hours; it is an amorphous substance, which dissolves very readily in water, and melts at 115°, evolving carbonic anhydride. Stollé obtained the same substance by hydrolysing ethylic phenyldihydroresorcinoldicarboxylate.

γ-Acetyl-β-phenylbutyric acid, $CH_2Ac\cdot CHPh\cdot CH_2\cdot COOH$, is obtained by hydrolysing phenyldihydroresorcinol and ethylic phenyldihydroresorcylate (compare Abstr., 1894, i, 528); the *ethylic* salt boils at 186—189° under a pressure of 20 mm., and is converted into phenyldihydroresorcinol under the influence of sodium ethoxide free from alcohol suspended in absolute ether. The *oxime* crystallises from water in lustrous plates, and melts at 127°, and the *lactone*,  $CHPh<\begin{matrix}CH_2\cdot CO\\ CH:CMe\end{matrix}>O$, has a peculiar odour, and boils at 177—180° under a pressure of 33 mm. The *amide* crystallises from water in small prisms containing $1H_2O$, and melts at about 128° when rapidly heated; the *amide anhydride* is obtained on heating the amide during several hours at 90—100°, and crystallises from water in long needles melting at 137°. The latter substance is also produced when ethylic acetylphenylbutyrate is heated in sealed tubes with alcoholic ammonia; nitrous acid converts the amide anhydride, $C_{12}H_{13}ON$, into the *compound* $C_{12}H_{14}O_3N_2$, which crystallises in small, white needles, melts and decomposes at about 188°, and does not give Liebermann's reaction. The *methylamide* of acetylphenylbutyric acid is obtained from the anhydride and methylamine and melts at 143°; the *methylamine* compound of the methylamide, $2C_{13}H_{17}O_2N + NH_2Me + H_2O$, crystallises in long needles, and yields the methylamide at 100°. The *anilide* crystallises from alcohol or acetic acid in leaflets, and melts at 135°.

The lactone of δ-hydroxy-β-phenylcaproic acid boils at 271—273° under a pressure of 17 mm. according to Michael and Freer, whilst Stollé states that the substance boils at 194—195° under a pressure of 13 mm.; the authors have prepared it by reducing γ-acetyl-β-phenylbutyric acid with sodium amalgam, and find that it boils at 190—192° under a pressure of 20 mm.

γ-Acetyl-β-anisylbutyric acid, $CH_2Ac\cdot CH(C_6H_4\cdot OMe)\cdot CH_2\cdot COOH$, is obtained by hydrolysing ethylic anisyldihydroresorcylate with barium hydroxide, and after crystallisation from water melts at 104°; the *oxime* melts at 169°.

γ-Benzoyl-β-phenylbutyric acid, $CH_2Bz \cdot CHPh \cdot CH_2 \cdot COOH$, is obtained by hydrolysing the crude salt produced from ethylic sodiomalonate and benzylideneacetophenone, and fusing the intermediate dibasic *acid*, $CH_2Bz \cdot CHPh \cdot CH(COOH)_2$, which melts and loses carbonic anhydride at 144°; the ketonic acid crystallises from glacial acetic acid in prisms and melts at 155—156°. The *oxime* melts at 144—146°, and a *lactone*,



$CHPh<\substack{CH_2 \cdot CO \\ CH{:}CPh}>O$ crystallises from ether in needles.

[With Karl Hobohm.]—*Isobutyrylanisylbutyric acid*,

$$CHMe_2 \cdot CO \cdot CH_2 \cdot CH(C_6H_4 \cdot OMe) \cdot CH_2 \cdot COOH,$$

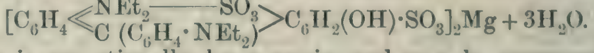
is obtained by fusing the acid, which arises from the action of ethylic sodiomalonate on anisylidenemethyl isopropyl ketone; it crystallises from acetic acid or boiling water, and melts at 118°. The *amide* crystallises from boiling water in slender, white needles, and melts at 158—159°. *Anisylidenemethyl isopropyl ketone*,

$$OMe \cdot C_6H_4 \cdot CH{:}CH \cdot CO \cdot CHMe_2,$$

is prepared from methyl isopropyl ketone and anisaldehyde under the influence of 10 per cent. caustic soda; it melts at 28° and boils at 217—219° under a pressure of 40 mm. M. O. F.

Molecular Rearrangement of Phenylsulphonamic Acid. By Eugen Bamberger and E. Hindermann (*Ber.*, 1897, **30**, 654—655).—Having shown that sulphurous anhydride converts phenylhydroxylamine into a mixture of phenylsuphonamic and orthamidobenzenesulphonic acids, an attempt was made to convert the former into the latter; by heating barium phenylsulphonamate at 180° during $4\frac{1}{2}$ hours, it is converted, however, into the barium salt of paramidobenzenesulphonic acid. M. O. F.

Constitution of "Patent Blue." By Ernst Erdmann and Hugo Erdmann (*Annalen*, 1897, **294**, 376—392. Compare Fritsch, this vol., i, 72).—Basing their conclusion on a synthesis which determines the position of at least one sulphonic group in the colouring matter, the authors ascribe to patent-blue, which they investigated in the form of its magnesium salt, the constitutional formula



$$[C_6H_4 \lll \substack{NEt_2 \text{———} SO_3 \\ C\ (C_6H_4 \cdot NEt_2)} > C_6H_2(OH) \cdot SO_3]_2Mg + 3H_2O.$$

The salt is exceptionally hygroscopic, and may be preserved many weeks in the exsiccator without becoming constant in weight; at 110°, however, upwards of 5 per cent. of moisture is removed, the remaining three molecules resisting a temperature of 160—170°, at which gradual decomposition occurs. Although the substance contains two sulphonic groups, it is not a hydrogen magnesium salt, because the composition remains unaltered after treatment with a boiling solution of barium hydroxide and subsequent saturation with carbonic anhydride.

Metahydroxytetrethylparadiamidotriphenylcarbinol,

$$OH \cdot C_6H_4 \cdot C(C_6H_4 \cdot NEt_2)_2 \cdot OH,$$

is obtained by heating patent-blue with concentrated hydrochloric acid during 66 hours in a reflux apparatus; it separates as a greenish precipitate on treatment with alkali as a dark green, amorphous powder, which forms a solution of the same colour in alcohol and in very dilute hydrochloric acid, the solution in excess of hydrochloric acid being yellow. The substance is indifferent towards hot caustic soda.

When patent-blue is treated with a boiling 5 per cent. solution of caustic soda, nitrogen is eliminated quantitatively as diethylamine, the liquid becoming violet, and finally red, owing to the production of a colouring matter of the rosolic acid series.

A colouring matter identical with the technical form of patent blue has been already synthesised by the authors (D. R. P., No. 46384) from metanitrobenzaldehyde and diethylaniline. The aldehyde and the base are heated with dehydrated oxalic acid during many hours on the water bath; the condensation product, metanitroleuco-brilliant-green is reduced with stannous chloride and hydrochloric acid, the amido-compound diazotised, and converted into hydroxyleuco-brilliant-green. The latter is treated with fuming sulphuric acid at ordinary temperatures, and finally oxidised with lead peroxide and sulphuric acid; the magnesium salt of the colouring matter obtained in this way exhibits all the properties of the technical form.

Whilst this process throws no light on the positions occupied by the sulphonic groups, a synthesis has been effected which shows that the free sulphonic radicle is in the para-position with regard to the carbon atom combined with the substituted aniline complexes. Nitration converts parachlorobenzaldehyde into parachlorometanitrobenzaldehyde, which yields sodium metanitrobenzaldehydeparasulphonate under the influence of sodium sulphite; reduction, diazotisation, and conversion into metahydroxybenzaldehydeparasulphonic acid then follow, the last-named condensing with diethylaniline to form metahydroxyleuco-brilliant-green-parasulphonic acid. When this substance is added to 5 parts of fuming sulphuric acid containing 20 per cent. of anhydride, a second sulphonic group is introduced, and the product yields patent-blue on oxidation with lead peroxide and sulphuric acid.

The *leuco-base of parachlorometanitro-malachite-green*,

$$NO_2\cdot C_6H_3Cl\cdot CH(C_6H_4\cdot NMe_2)_2,$$

is obtained by heating parachlorometanitrobenzaldehyde with dimethylaniline and zinc chloride on the water bath, and crystallises from alcohol in golden-yellow needles melting at 133—134°; it is oxidised by sulphuric acid and lead peroxide to a green colouring matter. The *leuco-base of parachlorometamido-malachite-green* crystallises from alcohol in white needles and melts at 167—167·5°.

Metanitroleuco-malachite-green-parasulphonic acid,

$$NO_2\cdot C_6H_3(HSO_3)\cdot CH(C_6H_4\cdot NMe_2)_2,$$

is obtained by the action of potassium sulphite on parachlorometanitroleuco-malachite-green, and also by condensing metanitrobenzaldehydeparasulphonic acid with dimethylaniline; the *sodium* salt crystallises in yellowish leaflets.

Metamidoleuco-brilliant-green-parasulphonic acid is obtained by heating potassium metanitrobenzaldehydeparasulphonate (2 parts) with diethylaniline (6 parts), zinc chloride (2 parts), and concentrated sulphuric acid (1 part), at first in the water bath, and finally at 110° during 14 hours; the product is rendered alkaline, freed from diethylaniline by a current of steam, and reduced with hydrochloric acid and zinc dust. On saturating the filtered liquid with ammonia, the *ammonium* salt of the sulphonic acid separates out; the *sodium* salt is crystalline.

Metahydroxyleuco-brilliant-green-parasulphonic acid,

$$OH\cdot C_6H_3(HSO_3)\cdot CH(C_6H_4\cdot NEt_2)_2,$$

is produced on diazotising the foregoing amido-compound, and eliminating nitrogen under the influence of heat; it is also obtained by heating sodium hydroxybenzaldehydesulphonate with dehydrated oxalic acid and diethylaniline at 110°. The substance is colourless, but rapidly becomes green when exposed to air; the *sodium* salt crystallises in leaflets. As already stated, when the sulphonic acid is added to fuming sulphuric acid, and the product oxidised with lead peroxide and sulphuric acid, patent-blue is formed.

The authors discuss the constitution of the colouring matter, and criticise the observations of Fritsch (*loc. cit.*). M. O. F.

Action of Nitrogen Oxides on Mercurydiphenyl and on Nitrosobenzene. By Eugen Bamberger (*Ber.*, 1897, **30**, 506—513).—The action of nitric oxide on mercurydiphenyl and similar substances was studied in the hope of synthesising nitroso-derivatives of aromatic hydroxylamines. Nitric oxide, however, in the absence of all traces of air, does not react with mercurydiphenyl, but in the presence of air small quantities of mercuryphenyl nitrate, $HgPh\cdot NO_3$, and of diazobenzene nitrate are formed.

Nitrous anhydride in chloroform solution readily reacts with mercurydiphenyl, even at low temperatures, yielding mercuryphenyl nitrate, diazobenzene nitrate, and nitrosobenzene. Nitric peroxide also readily reacts on mercurydiphenyl, the two products being mercuryphenyl nitrate and nitrosobenzene. As nitrosobenzene readily combines with nitric oxide, it follows that the nitrous anhydride reacts, at any rate to some extent, as a mixture of nitric oxide and peroxide. A second product was also obtained by the action of nitric oxide on nitrosobenzene. It is a yellow substance; the amount, however, was small, and it could not be obtained in a pure state.

Orthonitrosotoluene and parabromonitrosobenzene also react with nitric oxide, yielding orthodiazotoluene nitrate and parabromodiazobenzene nitrate respectively. It appears to be a characteristic property of all true nitroso-compounds to react with nitric oxide. Other aromatic derivatives of mercury appear to behave in much the same way as mercurydiphenyl.

The author suggests nitrosobenzene as a reagent for testing for nitric oxide or nitrous anhydride in nitric peroxide. J. J. S.

Zinc Dust in the Presence of Acetic Acid as an Oxidising Agent. By Ossian Aschan (*Ber.*, 1897, **30**, 657—658).—Sudborough (Trans., 1897, **219**) has shown that benzoin, when treated with zinc dust and acetic acid, yields benzil, an oxidation product of benzoin, together with deoxybenzoin. The author has observed a similar case of oxidation in the case of camphororthoquinone (Claisen and Manasse, Abstr., 1894, i, 479). A solution of the quinone (5 grams), in glacial acetic acid (30 grams) becomes quite hot on the addition of zinc dust, and the yellowish colour gradually disappears. When evaporated to half its bulk, and then treated with water, the solution yields camphoric anhydride, formed from the camphorquinone by oxidation. No appreciable quantity of any other substance could be isolated. J. J. S.

Action of Nitrosodimethylaniline on certain Bromo-derivatives of Gallic Acid. By ALEXANDRE BIÉTRIX (*Bull. Soc. Chim.*, 1896, [iii.], 15, 404—408).—By the action of nitrosodimethylaniline hydrochloride on dibromogallic acid, a blue substance is obtained, which appears to be *bromogallocyanin*, $C_{14}H_{11}NO_3ClBr\cdot COOH$.

Similarly, methylic dibromogallate gives, with nitrosodimethylaniline, the *methylic* salt of bromogallocyanin. In solution in water or alcohol, this has a violet colour, which turns red on the addition of an acid.

The anilide of dibromogallic acid gives, with nitrosodimethylaniline, the *anilide* of bromogallocyanin; it is a violet substance, soluble in alcohol, but only slightly so in water and benzene. M. W. T.

Action of Alphylhydrazines on β-Naphthaquinone. By EUGEN BAMBERGER (*Ber.*, 1897, 30, 513—516).—According to Zincke and Bindewald (Abstr., 1885, 391), the same product is obtained from α-naphthol and diazobenzene as from α-naphthaquinone and phenylhydrazine, whereas β-naphthol or β-naphthaquinone, when treated with the same reagents, yields two isomeric substances, which probably may be represented by the two formulæ $\underset{\beta}{O}\colon C_{10}H_6\colon \underset{\alpha}{N_2}HPh$ for the compound obtained from β-naphthol and diazobenzene, and $\underset{\alpha}{O}\colon C_{10}H_6\colon \underset{\beta}{N_2}HPh$, that from β-naphthaquinone and phenylhydrazine. The author now shows this view to be correct, since β-naphthaquinone and paranitrophenylhydrazine in acetic acid solution yield the same dye (m. p. 235—236°) which the author had previously prepared from α-naphthol and paranitrodiazobenzene, namely $O\colon C_{10}H_6\colon N_2H\cdot C_6H_4\cdot NO_2$ (compare Abstr., 1895, i, 351).

Similarly, β-naphthaquinone with paranitrophenylhydrazine and with orthonitrorthotolylhydrazine, yields the same dyes as have been previously obtained from α-naphthol (*loc. cit.*).

Paranitrorthotolylhydrazine was prepared by Bamberger and Kraus' method (Abstr., 1896, i, 610). On the addition of potassium sulphite to the solution of diazotised paranitrorthotoluidine, it yields a crystalline mass of *potassium paranitrorthotolylhydrazinesulphonate*,

$$NO_2\cdot C_6H_3Me\cdot N(SO_3K)\cdot NH\cdot SO_3K$$

$[Me : NO_2 : N = 2 : 4 : 1]$. This is then warmed on the water bath with concentrated hydrochloric acid, the precipitated crystals collected, dissolved in water, and the paranitrorthotolylhydrazine precipitated by the addition of sodium acetate. It crystallises from boiling alcohol or xylene in golden or orange-yellow needles, and melts at 179—180°.

J. J. S.

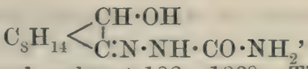
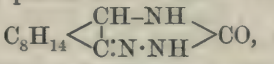
Camphor Leaf Oil. By DAVID HOOPER (*Pharm. J. Trans.*, 1896, [iv.], 2, 21—22).—The leaves of camphor trees from two different localities were distilled with water for 6 hours. The sample from Otacamund gave about 1 per cent. of essential oil, which was slightly yellow, had a sp. gr. = 0·9322 at 15°, and gave a rotation of + 9·4° in a 200 mm. tube; camphor was only present to the extent of about 10 or 15 per cent. Leaves from Naduvatam gave about 0·5 per cent. of

oil containing 75 per cent. of camphor dissolved and suspended in it. The strained oil had a sp. gr. = 0·9314 at 15°, and gave a rotation of + 54° in a 200 mm. tube.
R. R.

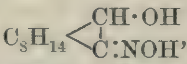
Hydroxycamphor. By OTTO MANASSE (*Ber.*, 1897, **30**, 659—670).—A number of compounds described as hydroxycamphor have been prepared by different chemists (compare Wheeler, *Annalen*, **146**, 83; Schiff, Abstr., 1880, 892; Kachler and Spitzer, Abstr., 1880, 324; Schrötter, Abstr., 1882, 66, and Schmiedeberg, *Zeit. Physiol. Chem.*, **3**, 422). The author, by the reduction of camphororthoquinone, has prepared yet another hydroxycamphor which in many respects resembles the compound described by Schmiedeberg as campherol, but differs altogether in its physiological action.

When camphorquinone prepared from isonitrosocamphor by means of nitrous acid is treated with zinc dust and acetic or sulphuric acid, it yields a mixture of hydroxycamphor and camphoric anhydride (see Manasse, this vol., i, 288), but camphorquinone prepared by the bisulphite method yields simply hydroxycamphor; the author thinks, therefore, that the camphoric anhydride was originally present as an impurity in the quinone obtained by the action of nitrous acid on isonitrosocamphor. A quantitative yield of hydroxycamphor may be obtained by the following method. The quinone is dissolved in ordinary ether, hydrochloric or sulphuric acid is added, and then, in small quantities at a time, zinc dust made into a cream with water, the mixture being well shaken until it becomes colourless. The acid solution, separated from the ethereal layer, is saturated with common salt and again extracted with ether. On distilling off the ether from the combined ethereal solutions, a white, crystalline compound is obtained, which is most conveniently purified by distillation with steam, or by recrystallisation from a little light petroleum. Either aluminium amalgam, or zinc dust and acetic acid may be used as the reducing agents; in the latter case, the temperature must not exceed 30—40°, as otherwise an oily bye-product is formed.

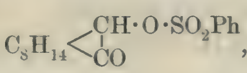
Hydroxycamphor purified by distillation in steam is a snow-white, practically odourless powder. It melts at 203—205°, and is soluble in cold water to the extent of about 2 per cent.; it melts in hot water and is fairly readily soluble on boiling, separating again in a crystalline form as the solution cools. It can easily be "salted out" from its aqueous solutions, and is extremely soluble in all organic solvents with the exception of light petroleum. Although not so readily volatile as either camphor or camphorquinone, it is yet volatile to a slight extent with ether vapour. Its solutions are dextrorotary, the specific rotation being + 9·5°. It does not form salts with alkalis, although it is sparingly soluble in caustic soda solution. On oxidation with an acetic acid solution of chromic anhydride, it is converted into camphorquinone; with hydrogen peroxide in alkaline solution, however, it yields camphoric acid. The latter process of oxidation takes place much more slowly than the similar oxidation of camphorquinone to camphoric acid. The physiological properties of the compound are given in detail; its chief action appears to be a slackening of the respiratory function.

Hydroxycamphorsemicarbazone,  $C_8H_{14}<\begin{array}{l}CH\cdot OH\\ C{:}N\cdot NH\cdot CO\cdot NH_2\end{array}$, crystallises in hard, glistening prisms and melts at 182—183°. The corresponding *anhydride* (?)  $C_8H_{14}<\begin{array}{l}CH{-}NH\\ C{:}N\cdot NH\end{array}>CO$, which is sometimes formed together with the semicarbazone, melts and decomposes at 208—209°.

Hydroxycamphorphenylhydrazone crystallises from dilute alcohol in yellowish needles, and melts at 137·5°.

Hydroxycamphoroxime (isonitrosoborneol),  $C_8H_{14}<\begin{array}{l}CH\cdot OH\\ C{:}NOH\end{array}$, crystallises from a mixture of ether and light petroleum, or from aqueous alcohol, in splendid, glistening pyramids. It melts at 86—87° and contains $\frac{1}{2}H_2O$; when anhydrous it melts at 121—122°.

Benzoyl and *acetyl* derivatives of hydroxycamphor could only be obtained in the form of syrups.

Hydroxycamphorphenylsulphone,  $C_8H_{14}<\begin{array}{l}CH\cdot O\cdot SO_2Ph\\ CO\end{array}$, crystallises in pyramids and melts at 95—96°. J. J. S.

High Boiling Point Constituents of Oil of Celery. By GIACOMO L. CIAMICIAN and PAUL G. SILBER (*Ber.*, 1897, 30, 492—501).—A small portion of the high boiling point oil and residue obtained on distilling celery seed oil is soluble in alkali, and consists of palmitic acid together with substances of phenolic character, one of which crystallises in broad, white needles, melts at 66—67°, and has the formula $C_{16}H_{20}O_3$.

The remainder of the oil may be divided into two portions by boiling with 25 per cent. aqueous potash, the insoluble residue consisting of terpene-like compounds of the composition $C_{15}H_{24}$, whilst the solution is found to contain two acids. The first of these, *sedanolic acid,* $C_{12}H_{20}O_3$, very readily forms a lactone, and may thus be separated from the *sedanonic acid* which accompanies it.

Sedanolic acid can only be obtained pure by acidifying the alkali solution of the acid at a low temperature, dissolving the acid in ether, and precipitating it from this solution by adding light petroleum; it crystallises in white needles, is insoluble in water, and melts at 88—89°. A solution of the acid in sodium carbonate at once reduces potassium permanganate solution. The *silver* salt has the normal composition.

The lactone, *sedanolide,* $C_{12}H_{18}O_2$, prepared by distilling the acid, boils at 185° (under a pressure of 17 mm.). It is a thick, colourless oil, and is the odoriferous constituent of oil of celery, in which it appears to occur in the free state. Its constitution has not yet been definitely ascertained.

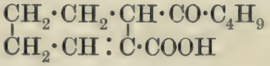
Sedanonic acid, $C_{12}H_{18}O_3$, is insoluble in water, and crystallises from benzene in compact, white crystals melting at 113°; the *silver* salt is soluble in hot water. It is a well-marked ketonic acid, the *phenylhydrazone* of which is extremely unstable, and melts at 130—131°; the *oxime,* $C_{12}H_{18}O_2{:}NOH$, is a stable substance which separates from benzene in white crystals having a fatty lustre and melting at 128°. A. H.

Products of Decomposition of Sedanonic Acid. By Giacomo L. Ciamician and Paul G. Silber (*Ber.*, 1897, **30**, 501—506. Compare the preceding abstract).—When sedanonoxime is warmed with concentrated sulphuric acid, it undergoes molecular change and is converted into Δ^2-*Tetrahydrophthalo-n-butylamic acid*,

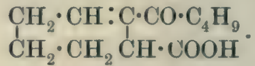
$$COOH\cdot C_6H_8\cdot CO\cdot NH\cdot C_4H_9,$$

which crystallises in colourless prisms melting at 171°; this compound, when heated with dilute sulphuric acid, undergoes hydrolysis, yielding *n*-butylamine and Δ^2-tetrahydrophthalic acid (Baeyer, Abstr., 1890, 1275), which was recognised by its properties and by the fact that on reduction it was converted into the fumaroid form of hexahydrophthalic acid.

Sedanonic acid itself, therefore, probably has one of the two following formulæ.



$$\begin{array}{l} CH_2\cdot CH_2\cdot CH\cdot CO\cdot C_4H_9 \\ CH_2\cdot CH\colon C\cdot COOH \end{array}$$



$$\begin{array}{l} CH_2\cdot CH\colon C\cdot CO\cdot C_4H_9 \\ CH_2\cdot CH_2\,CH\cdot COOH \end{array}.$$

A. H.

Luteolin. By Josef Herzig (*Ber.*, 1897, **30**, 656. Compare this vol., i, 94).—The bye-product obtained in preparing luteolin triethyl ether is colourless, and melts at 146—149°; it is probable that this substance is tetrethylluteolin. M. O. F.

Cochineal Dye. By Carl T. Liebermann and Hugo Voswinckel (*Ber.*, 1897, **30**, 688—691).—The dye stuff obtained from 1 kilo. of cochineal or from 150 grams of cochineal-carmine was dissolved in 3 litres of acidified water, and to this solution 125 grams of potash dissolved in 250 c.c. of water was first added, and then 100 grams of potassium persulphate mixed with water, when the violet colour gradually changed to yellowish-brown. The liquid was then filtered from precipitated inorganic salts, the filtrate acidified, evaporated to one-sixth its volume, and extracted several times with ether containing a small quantity of alcohol; on distilling off the ether, a solid residue was obtained containing several organic acids. The yield is not good, but is much better when smaller quantities of the cochineal dye are operated on at a time. The aqueous solution of the residue, when boiled with animal charcoal and allowed to cool, deposited a small quantity of needle-shaped crystals of a sparingly soluble acid which the author terms coccinic acid. The amount of this is about one-tenth of the total ethereal residue.

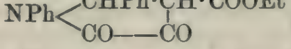
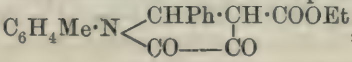
Coccinic acid, $C_9H_8O_5$(?), is only sparingly soluble in water, but dissolves readily in alcohol. It melts and decomposes at 293°.

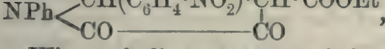
On treating the filtrate from the coccinic acid with lead acetate, it yields a precipitate consisting of the lead salt of a new acid, which is termed cochinelic acid.

Cochinelic acid, $C_{10}H_8O_7$(?), is moderately soluble in cold water, readily in hot, and extremely so in alcohol, glacial acetic acid or acetone; benzene, aromatic hydrocarbons, and ether, however, dissolve it but sparingly, whilst in light petroleum, chloroform or carbon bisulphide it is practically insoluble. It crystallises in small needles and melts at 224—225°, carbonic anhydride being evolved at the same time. The *calcium* salt, which is readily soluble in water, apparently has the composition $C_{10}H_6O_6Ca$.

With ferric chloride, it gives a red coloration, indicating the presence of phenolic hydroxyl groups, and with bromine water it yields a *tribromocresotic acid*, $OH\cdot C_6Br_3Me\cdot COOH$, which melts at 220°.

J. J. S.

Synthesis of Ethereal Salts of Substituted Diketodihydropyrrolinecarboxylic Acids by means of Ethylic Oxalacetate and Aldehydoamido-Bases. By ROBERT SCHIFF and C. BERTINI (*Ber.*, 1897, **30**, 601—604).—When ethylic oxalacetate is heated with benzylideneaniline, or benzaldehyde and aniline, *ethylic* 1 : 2-*diphenyldiketodihydropyrroline-3-carboxylate*,  $\mathrm{NPh}<\begin{array}{l}\mathrm{CHPh\cdot CH\cdot COOEt}\\ \mathrm{CO{-}{-}{-}CO}\end{array}$, is formed. It crystallises well and melts at 171°; with sodium ethoxide, it yields a *sodium* compound, $C_{19}H_{16}NaNO_4$. Two *isomeric monoximes* have been prepared; one of these is almost insoluble in ether and melts at 224°; the other is readily soluble and melts at 110°. Similar compounds have been obtained from a number of amido-compounds. Paratoluidine yields a *substance*,  $\mathrm{C_6H_4Me\cdot N}<\begin{array}{l}\mathrm{CHPh\cdot CH\cdot COOEt}\\ \mathrm{CO{-}{-}{-}CO}\end{array}$, which melts at 152—153°.

The *compound* from metanitraniline, $NO_2\cdot C_6H_4\cdot C_4NH_2PhO_2\cdot COOEt$, melts at 199—200°, and $C_{10}H_7\cdot C_4NH_2PhO_2\cdot COOEt$, that from β-naphthylamine, at 142—143°. The *substance* obtained from amidoazobenzene, $N_2Ph\cdot C_6H_4\cdot C_4NH_2Ph\cdot COOEt$, forms crystals which are insoluble in alcohol, and melt at 215°, whilst that from metamidobenzoic acid, $COOH\cdot C_6H_4\cdot C_4NH_2PhO_2\cdot COOEt$, melts at 230°. Ethylic acetate, aniline, and metanitrobenzaldehyde yield a *substance*,  $\mathrm{NPh}<\begin{array}{l}\mathrm{CH(C_6H_4\cdot NO_2)\cdot CH\cdot COOEt}\\ \mathrm{CO{-}{-}{-}{-}{-}{-}CO}\end{array}$, which melts at 208—209°.

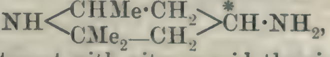
When ethylic acetoacetate is heated with a little alcohol and a molecular proportion of benzylideneaniline, an additive compound,

$$NHPh\cdot CHPh\cdot CHAc\cdot COOEt,$$

is formed which melts at 103—104°, and is readily decomposed by acids.

A. H.

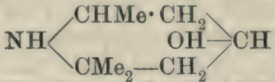
Stereochemical Researches in the Piperidine Series. By CARL D. HARRIES (*Annalen*, 1897, **294**, 336—375. Compare Abstr., 1896, i, 317).—By the investigation of 4-amido-2 : 2 : 6-trimethylpiperidine, obtained on reducing vinyldiacetonamidoxime (*loc. cit.*), an interesting case of stereochemical isomerism has been brought to light. The base in question, having the constitutional formula



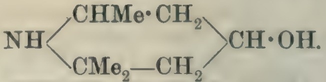
$$\mathrm{NH}<\begin{array}{l}\mathrm{CHMe\cdot CH_2}\\ \mathrm{CMe_2{-}CH_2}\end{array}>\overset{*}{\mathrm{C}}\mathrm{H\cdot NH_2},$$

should yield, on treatment with nitrous acid, the vinyldiacetonalkamine (m. p. 123°) obtained by E. Fischer on reducing vinyldiacetonamine; in preparing vinyldiacetonalkamine, however, in order to compare it with the product of the action of nitrous acid on the amidopiperidine derivative, it was found that on working with large quantities of substance at a higher temperature, an isomeric vinyldiacetonalkamine is produced melting at 160—161°. As this compound might also arise from the action of nitrous acid on an amidotrimethylpiperidine isomeric with the derivative already obtained on reducing vinyldiacetonamidoxime with zinc dust and alcoholic hydrochloric acid at temperatures below 10°, the oxime was reduced with sodium and boiling amylic alcohol; in this way, an isomeric 4-amido-2 : 2 : 6-trimethylpiperidine is produced which, on treatment with nitrous acid, yields the new vinyldiacetonalkamine melting at 160—161°.

The isomerism under discussion is doubtless due to the carbon atom indicated by an asterisk in the foregoing formula, and in this respect is analogous to that recognised by Willstätter (Abstr., 1896, i, 451) as existing between tropine and ψ-tropine, the latter of which is produced on treating the former with hot sodium amyloxide; on endeavouring to convert one vinyldiacetonalkamine into the other under the influence of the same agency, it was found that both forms (m. p. 120—121° and m. p. 160—161°) yield a third modification which melts at 137—138°. Careful investigation of these three substances has shown that the form which melts at 137—138° is the stable modification of the form melting at 160—161°, the third substance (m. p. 120—121°) being an intimate mixture of both isomerides; the author refers to them as the α- and β-modifications respectively, and represents them by the following expressions:



α-Vinyldiacetonalkamine (stable)
m. p. 137—138°.

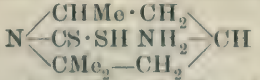


β-Vinyldiacetonalkamine (labile)
m. p. 160—161°.

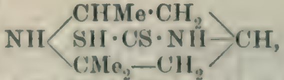
Although the mixture which melts at 120—121° does not represent a third modification, it closely simulates an individual substance crystallising in beautiful, six-sided prisms which are quite distinct from the cubes melting at 137—138° and the long, lustrous prisms which melt at 160—161°; it is not possible, moreover, to resolve the mixture of bases by repeated crystallisation from benzene, an operation which does not raise the melting point above 120—121°, and the author is disposed to regard as probable the existence of some form of combination, more especially as 4-amido-2 : 2 : 6-trimethylpiperidine, which is certainly an individual substance, yields the characteristic crystals of the mixture when treated with nitrous acid.

The isomerism of the two amidotrimethylpiperidines is of the same character as that of the vinyldiacetonalkamines, the form already described (Abstr., 1896, i, 318) constituting the α-modification, whilst the base obtained on reducing the oxime with sodium and boiling amylic alcohol is the β-isomeride; the former of these yields, with carbon bisulphide, the α-thiocarbamate,

a,



b,

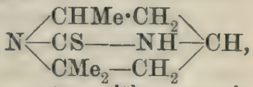


which melts at 144—145°, and when treated with boiling water yields the *b*-thiocarbamate which melts at 187—188° (*loc. cit.*), whilst the β-modification yields a single thiocarbamate which melts at 197—198°.

Vinyldiacetonamidoxime *dihydrochloride* is obtained on adding ether to an alcoholic solution of the oxime which has been saturated with hydrogen chloride; it is very hygroscopic, and when heated at 100° yields the *monhydrochloride* which crystallises from absolute alcohol in leaflets.

The α-modification of 4-amido-2 : 2 : 6-trimethylpiperidine is obtained, as already stated (*loc. cit.*), by reducing vinyldiacetonamidoxime with zinc dust and alcoholic hydrogen chloride at temperatures below 5°; in order to separate it from the isomeride which is also produced, the mixed hydrochlorides are treated with absolute alcohol, in which the hydrochloride of the β-modification is insoluble. When the base is treated in ethereal solution with carbon bisulphide (1 mol.), the *a-thiocarbamate*, $C_9H_{18}N_2S_2$, is obtained as a hygroscopic substance which melts and decomposes at 144—145°; it is excessively soluble in water, and mercuric chloride gives with the solution a bright orange precipitate, which gradually becomes white when heated, and although mercuric sulphide is not precipitated under these circumstances, the compound at once separates when a hot solution of the mercuric salt is added to the hot aqueous thiocarbamate. This is due to the production of the *b*-thiocarbamate, which is formed when an aqueous solution of the *a*-modification is boiled, and crystallises in lustrous prisms melting at 187—188° (*loc. cit.*); mercuric chloride gives a reddish precipitate with the aqueous solution, becoming black when heated.

a-Amidotrimethylpiperidine eso-thiocarbamide,

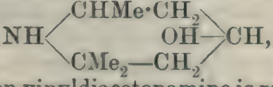


$N\left\langle\begin{matrix}CHMe\cdot CH_2\\ CS\text{——}NH\\ CMe_2\text{—}CH_2\end{matrix}\right\rangle CH$,

the substance obtained on treating the thiocarbamates with mercuric chloride, melts at 77—78° (compare *loc. cit.*); the *hydrochloride* melts and decomposes at 254—255°, and the *aurochloride* crystallises in yellow, oblique prisms which melt and decompose at 108—109°.

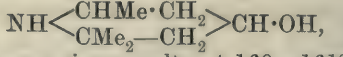
The *β-modification* of 4-amido-2 : 2 : 6-trimethylpiperidine is obtained by dissolving vinyldiacetonamidoxime in hot amylic alcohol and adding sodium in small pieces to the boiling solution; it is a colourless liquid which boils at 82—84° under a pressure of 22 mm. The *hydrate* crystallises in beautiful, transparent plates, melts at 20°, and boils at 91—92° under a pressure of 22 mm.; the *hydrochloride* and *hydrobromide* are crystalline, the *aurochloride* resembles that of the α-modification, the *platinochloride* forms fascicular groups of long needles, and the *picrate* crystallises in rhombic prisms. The *acetyl* derivative melts at 85—86°; the *acetate* of this base melts and decomposes at 130—132°, and the *aurochloride* crystallises in beautiful, concentric groups of leaflets. Carbon bisulphide converts β-amidotrimethylpiperidine into a *thiocarbamate*, $C_9H_{18}N_2S_2$, which crystallises in small, six-sided prisms and melts at 197—198°; when the aqueous solution is boiled, hydrogen sulphide is evolved, and β-amidotrimethylpiperidine is regenerated, along with a very small quantity of an oil which crystallises.

a-Vinyldiacetonalkamine,



$NH\left\langle\begin{matrix}CHMe\cdot CH_2\\ OH\\ CMe_2\text{—}CH_2\end{matrix}\right\rangle CH$, is produced along with the β-modification when vinyldiacetonamine is reduced with sodium amalgam, and crystallises from benzene in regular cubes melting at

137—138° and boiling at 211°; the *hydrochloride* crystallises in prisms, and the *aurochloride* and *platinochloride* crystallise in large, yellow, rectangular plates.



β-Vinyldiacetonalkamine, $NH{<}\begin{matrix}CHMe\cdot CH_2\\ CMe_2—CH_2\end{matrix}{>}CH\cdot OH$, crystallises from benzene in silky, lustrous prisms, melts at 160—161°, and boils at 204—205°; the *hydrochloride* is an oil, the *aurochloride* crystallises in beautiful, yellow plates, and the *platinochloride* in fascicular needles. Sodium amyloxide converts it into the α-modification. M. O. F.

Syntheses in the Piperidine Series. By FELIX B. AHRENS (*Ber.*, 1897, **30**, 533—537).—The compound $C_{10}H_{20}N_2$, obtained by the electrolysis of nitrosopiperidine, and described in a previous paper as dipiperidyl, was evidently not quite pure, as on recrystallising it from acetone, large, transparent crystals melting at 96—97°, and corresponding in composition with *diperideine*, $C_{10}H_{18}N_2$, are obtained. The *monobenzoyl* derivative of this compound melts at 145—147°.

Reduction of diperideine with tin and hydrochloric acid gives rise to two isomeric compounds, separable by means of their platinochlorides; on adding platinic chloride to the acid reduction product after it has been freed from tin by hydrogen sulphide, an orange-yellow, crystalline precipitate is instantly formed, which, on recrystallisation from water, yields the pure *platinochloride*, $(C_5H_{11}N),H_2PtCl_6 + 2H_2O$, in microscopic needles melting at 253—254°. The corresponding *aurochloride* forms needles melting and decomposing at 195°, the *free* base obtained, on adding potassium hydroxide to a solution of the hydrochloride and extracting with ether, although yielding a solid carbonate when its ethereal solution is saturated with carbonic anhydride, has not as yet been obtained in a crystalline condition.

On concentrating the filtrate from the platinochloride first precipitated, red, flat crystals of an isomeric *platinochloride*, $(C_5H_{11}N),H_2PtCl_6 + 2H_2O$, separate; this melts at 220°, and at 230° effervesces vigorously. The corresponding *aurochloride* forms large needles melting and decomposing at 218°—219°. The *hydrochloride*, $C_5H_{11}N,HCl$, consists of needles stable at 280°; the *hydrobromide*, which also crystallises in needles, does not melt below 270°, the corresponding *base*, which, like its isomeride, forms a solid carbonate, is an oil becoming partially crystalline when kept for a long time.

The matter is still under investigation, the author proposing to further study the behaviour of homologues of nitrosopiperidine under the same conditions. J. F. T.

Tetrahydroquinoline-1-sulphonic Acid. By ADOLPH CLAUS and WILHELM GÜNTHER (*J. pr. Chem.*, 1897, [ii], **55**, 94—112).—*Tetrahydroquinoline-1-sulphonic acid*, which is best prepared by reducing quinoline-1-sulphonic acid with tin and hydrochloric acid, forms fascicular groups of slender crystals and decomposes at 240—242°. It yields well crystallised salts, of which the *potassium*, *barium*, *calcium*, *copper*, and *silver* salts have been prepared. *Methylic tetrahydroquinoline-1-sulphonate methiodide* is obtained by heating the silver salt with methylic iodide, but very readily loses hydrogen iodide, and passes into *methyltrihydroquinoline*-1-*sulphonic methylbetaine*, which crystallises in hard, vitreous prisms melting at 251°.

When tetrahydroquinolinesulphonic acid is fused with potash, the sole product is 1-hydroxyquinoline. The sulphonic group is best removed by distilling the ammonium salt with ammonium chloride in a current of ammonia. When heated with hydrochloric acid, quinoline is formed together with a base which contains sulphur, but has not yet been obtained pure.

When the sulphonic acid is treated with bromine in presence of water, derivatives of quinoline and quinolinesulphonic acid are always obtained, together with bromotetrahydroquinolinesulphonic acid; the chief products under such circumstances are 1-bromoquinoline; a compound melting at 101°, which is probably 1 : 3-*dibromoquinoline*; 1 : 3 : 3′-tribromoquinoline (in largest amount), and a *tetrabromoquinoline* which melts at 255°, and is also formed by the further bromination of 1 : 3 : 3′-tribromoquinoline. In addition to these, quinolinesulphonic acid itself and its *monobromo*-derivative, which crystallises in red needles and does not melt below 360°, are also formed. On the other hand, when the bromination is carried out in chloroform solution, 3-bromotetrahydroquinoline-1-sulphonic acid is formed almost quantitatively; this crystallises in slender, lustrous needles melting at 245°. The constitution of this acid has not been definitely settled, but since it yields 1 : 3 : 3′-tribromoquinoline on further bromination in aqueous solution, most probably it has the one assigned to it above. The *ammonium*, *potassium*, *silver*, *calcium*, *barium*, *cobalt*, *nickel*, and *lead* salts have all been prepared. When the silver salt is heated with methylic iodide, 3-*bromomethyltrihydroquinoline*-1-*sulphonic methylbetaine*, $C_9H_8BrNMe_2(SO_3)$ is produced; this crystallises in long, colourless needles and melts at 253°.

When the brominated acid is fused with potash, it yields 1-hydroxyquinoline.

The acid previously described as 4-bromoquinoline-2-sulphonic acid is in reality 3-bromoquinoline-1-sulphonic acid, since on reduction it yields tetrahydroquinoline-1-sulphonic acid. A. H.

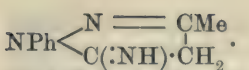
Constitution of the Compounds of Antipyrin with Phenols. By Gustave Patein (*Compt. rend.*, 1897, **124**, 233—235).—Phenylmethylpyrazolone does not form combinations with β-naphthol, resorcinol, quinol, or salicylic acid in presence of alcohol. It follows that in the case of antipyrin it is the more electropositive nitrogen 2 that combines with the phenols, and the formation of the compounds cannot be reconciled with E. von Meyer's view that the constitution of antipyrin is of the same general character as that of the betaines.

C. H. B.

Dinitrilophenylhydrazones and the Products of their Intramolecular Change. By Reinhold Walther (*J. pr. Chem.*, 1897, [ii], **55**, 137—144).—When the phenylhydrazone of diacetonitrile,

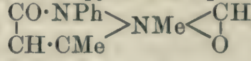
$$CN\cdot CH_2\cdot CMe{:}N\cdot NHPh,$$

melting at 97°, is heated with hydrochloric acid, it is converted into an isomeric substance which crystallises in compact prisms and melts at 116°. This isomeride appears to be 1-*phenyl*-3-*methyl*-5-*imidopyrazolone*,


$NPh<\begin{matrix}N = CMe \\ C(:NH)\cdot CH_2\end{matrix}$. If the original hydrazone melting at 97° is treated in alcoholic solution with gaseous nitrous acid, it yields a *nitroso* derivative, $C_{10}H_{10}N_4O$, which crystallises in carmine red, lustrous prisms melting at 195—196°; this substance, when heated with alcoholic hydrochloric acid at 120°, is converted into Knorr's 1-phenyl-3-methyl-4-isonitroso-5-pyrazolone (*Annalen*, **238**, 185), and the same compound is obtained by the direct action of sodium nitrite and hydrochloric acid on the above-mentioned isomeride of the hydrazone (m. p. 116°).

The results obtained above show that the isomeride produced from the hydrazone of diacetonitrile has a constitution analogous to that proposed by Burns (Abstr., 1893, i, 314) for the corresponding isomeride of diacetonitrileoxime. A. H.

A Condensation Product of Formaldehyde with Antipyrine. By E. MARCOURT (*Bull. Soc. Chim.*, 1896, [iii], **15**, 520).—When a solution containing equivalent quantities of antipyrine and formaldehyde is allowed to stand for a few days, a crystalline substance is deposited which appears to be a direct condensation product of the two substances. *Formopyrine* forms crystals which belong to the monoclinic system and melts at 142°. It is slightly soluble in hot water, insoluble in ether and benzene, and soluble in alcohol. In moist air, it appears to be stable at the ordinary temperature, but when heated to 110°, or if kept in a vacuum, the crystals decrepitate and lose formaldehyde. Formopyrine acts as a weak base, forming the salts $C_{12}H_{14}N_2O_2,HCl$, $(C_{12}H_{14}N_2O_2)_2,H_2SO_4$, $C_{12}H_{14}N_2O_2,H_2SO_4$, $C_{12}H_{14}N_2O_2,HNO_3$, $C_{12}H_{14}N_2O_2,H_3PO_4$, $C_{12}H_{14}N_2O_2,C_2H_2O_4$, which are white, crystalline substances.

The author considers that formopyrine has probably the constitution represented by the formula  $\begin{matrix}CO\cdot NPh \\ CH\cdot CMe\end{matrix}>NMe<\begin{matrix}CH_2 \\ O\end{matrix}$ from analogy with a similar compound formed by the condensation of antipyrine with chloral. M. W. T.

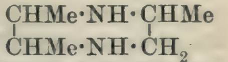
Dimethylpyrazine. By FELIX B. AHRENS and GEORG MEISSNER (*Ber.*, 1897, **30**, 532—533).—Ten grams of isonitrosoacetone was dissolved in 200 grams of sulphuric acid (5 per cent.) and placed in a porous cell, which in its turn was surrounded by sulphuric acid of the same strength. Platinum foil was used as the anode, and lead foil as the cathode. The density of the cathode current was 3—7 ampères per 100 sq. cm., and the voltage 4—6. The complete electrolysis required 3—5 hours, the product was then extracted with ether, rendered alkaline, and distilled so long as the distillate was still strongly alkaline. The distillate was then acidified with hydrochloric acid and precipitated with mercuric chloride. The precipitate, when dissolved in water, treated with hydrogen sulphide, and then rendered alkaline, gave the free base, dimethylpyrazine or ketine, which was extracted with ether. J. J. S.

Pyrazines and Piperazines. VII. By CARL STOEHR (*J. pr. Chem.*, 1897, [ii], **55**, 49—77. Compare Abstr., 1893, i, 486).—The pyrazines are converted by reduction directly into piperazines, no intermediate di- or tetra-hydropyrazines having been observed. The piperazines, which closely resemble the aliphatic diamines, are obtained in two modifications, which are probably stereoisomerides, one form being produced in small amount only. The rise of boiling point produced in the pyrazines by the introduction of a methyl group is 18°, whereas in the piperazine series it is only about 7°, hence, although the lower members of the piperazine series boil at higher temperatures than the corresponding pyrazines, the reverse is the case with the higher members. Of the two isomeric forms of the piperazines, the β-modification, that which is produced in smaller amount, usually has a slightly higher boiling point, does not crystallise so well, and yields a hydrochloride which is more readily soluble in alcohol than that of the α-form.

α-2 : 5-Dimethylpiperazine has previously been described; it crystallises in tabular forms of the monosymmetric system

$$[a:b:c = 1\cdot7026:1:2\cdot9809.\ \beta = 86°\ 34'].$$

β-2 : 5-*Dimethylpiperazine* crystallises less readily than the α-compound and forms rhombic tablets; $a:b:c = 1\cdot6534:1:2\cdot7416$. It melts at 114—115°, 4° below the α-compound, and boils at the same temperature as the latter, namely, 162°. The *hydrochloride*, $C_6H_{14}N_2,2HCl + H_2O$, is much more readily soluble in water and alcohol than that of the α-compound; the *hydrobromide*, $C_6H_{14}N_2,2HBr + H_2O$ forms prismatic, rhombic crystals which lose their water at 110—120° and then melt at 287—288°; the *sulphate* forms lustrous tablets; the *dichromate* deflagrates at 140—141° and closely resembles the α-compound, forming tabular, asymmetric crystals. The *phosphate*, $C_6H_{14}N_2,2H_3PO_4 + H_2O$, crystallises in asymmetric prisms. The *tartrate*, $C_6H_{14}N_2,C_4H_6O_6 + 1\frac{1}{2}H_2O$, crystallises in needles or irregular prisms, the anhydrous salt melting at 222—223°. The *picrate* is almost insoluble in cold water. The *dibenzoyl* derivative melts at 147—148° (previously stated as 151—152°) and crystallises in monosymmetric prisms.

II. [With P. Brandes.]—α-*Trimethylpiperazine*, 
$$\begin{array}{l}\text{CHMe·NH·CHMe}\\ \quad| \qquad\qquad\quad |\\ \text{CHMe·NH·CH}_2\end{array}$$
boils at 169—169·5°, and when cooled with ice, solidifies in lustrous prisms; the *hydrochloride*, which crystallises in lustrous tablets and decomposes above 270° without melting, is only sparingly soluble in boiling alcohol; the *platinochloride* crystallises with $2H_2O$; the *picrate* decomposes at 278—279°. The *dibenzoyl* derivative forms anhydrous, rhombic tablets and melts at 190°. The *dinitrosamine*, $C_7H_{14}N_2(NO)_2$, crystallises in almost colourless plates, melting at 95—96°.

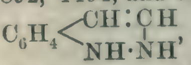
β-2 : 3 : 5-*Trimethylpiperazine* boils at 174—175° and could not be obtained in the solid form; the *hydrochloride* is readily soluble in alcohol and only crystallises with difficulty; the *platinochloride* crystallises with $2H_2O$ in four-sided prisms; the *picrate* melts and decomposes at 246°. The *dibenzoyl* derivative and the dinitrosamine could not be obtained in the solid form.

III. [With W. Detert; compare Abstr., 1893, i, 486].—α-2 : 5 : 3-*Dimethylethylpiperazine* boils at 176° and is difficult to obtain free from water; when cooled with ice, it solidifies to a colourless, crystalline mass. The *dibenzoyl* derivative crystallises in colourless, lustrous tablets, and melts at 169°.

β-2 : 5 : 3-*Dimethylethylpiperazine* boils at 185—186°, and, like the α-base, cannot readily be obtained quite free from water. It does not solidify at 0°; the *hydrochloride* is readily soluble in alcohol and crystallises with difficulty; the *platinochloride* crystallises with $2H_2O$ in lustrous plates; the *picrate*, which crystallises with $\frac{1}{2}H_2O$, melts and decomposes at 250°. The dinitrosamine and dibenzoyl derivative were obtained as oily liquids.

IV. [With P. BRANDES; compare Abstr., 1896, i, 576].—*α-Tetramethylpiperazine* (compare Wolff, Abstr., 1893, i, 373) crystallises in colourless, slender needles, boils at 177°, and melts at 37°; the *hydrochloride* is very sparingly soluble in alcohol. The *dinitrosamine* crystallises in colourless prisms and melts at 157°. The *dibenzoyl* derivative crystallises in colourless, lustrous tablets, and melts at 242°. The *picrate* and the *mercurochloride* are sparingly soluble in water.

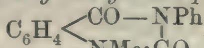
β-Tetramethylpiperazine boils at 181° and could not be obtained in the solid form; the *hydrochloride* is moderately soluble in alcohol and forms slender needles. The *dinitrosamine*, which crystallises in small colourless needles, can be sublimed without decomposition and melts at 101°. The *dibenzoyl* derivative crystallises in colourless, lustrous prisms melting at 175°. A. H.

Cinnoline. By MAX BUSCH and ALBERT RAST (*Ber.*, 1897, **30**, 521—527. Compare Busch and Klett, Abstr., 1892, 1494, and von Richter, Abstr., 1883, 1105).—*Dihydrocinnoline*,  $C_6H_4<\begin{matrix}CH:CH\\ NH\cdot NH\end{matrix}$, is best obtained by dissolving 5 grams of chlorocinnoline (*loc. cit.*) in 100 grams of sulphuric acid (15 per cent.) and then adding 5 grams of iron filings; the mixture is kept well shaken, and the reduction is complete at the end of 2 hours. Any filings that may be left are filtered off, the filtrate rendered neutral with solid soda, and then extracted several times with ether; the yellow crystals obtained by distilling off the greater part of the solvent are recrystallised from light petroleum. The substance crystallises in colourless plates, melts at 87—88°, and can be distilled without undergoing decomposition. It is but slightly basic, its salts being instantaneously decomposed by water, and it has an odour somewhat similar to that of naphthylamine. Reducing agents have no action on the base. The *hydrochloride*, $C_8H_8N_2,HCl$, crystallises from its concentrated alcoholic solution in flat, glistening needles, melts and decomposes at 149—150°, and when not quite pure readily turns brown on exposure to the air. No platinochloride could be obtained. The *sulphate*, $C_8H_8N_2,H_2SO_4$, resembles the hydrochloride.

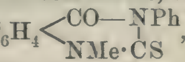
Cinnoline (*α-phenoiazine*), $C_6H_4<\begin{matrix}CH:CH\\ N{=}N\end{matrix}$, is best obtained by oxidising dihydrocinnoline (1 part) dissolved in benzene with freshly prepared mercuric oxide (20 parts); as the oxidation takes place but slowly, it is necessary to warm the mixture for 3 hours on the water bath. The base is best purified by means of its *hydrochloride*, which separates in green or brownish, glistening needles on adding ether to the alcoholic solution; it is readily soluble in water and alcohol, begins to sublime at 100°, softens at 156°, and melts at 160°. The *base* is obtained as an oil on adding sodium hydroxide to the hydrochloride. In the cold, it crystallises from light petroleum in small, glistening, compact crystals which melt at 39°, and from ether in colourless, glistening needles which contain 1 molecule of ether of crystallisation and melt at 24—25°. Cinnoline is a strong base, and is readily soluble in most solvents, even in water. It possesses a characteristic odour somewhat resembling that of geraniums, has an extremely bitter taste, is poisonous, and decomposes slightly when distilled.

The *picrate*, $C_8H_6N_2,C_6H_2(NO_2)_3\cdot OH$, crystallises in amber-yellow prisms, melts at 190°, and is sparingly soluble in alcohol but insoluble in water. The *platinochloride*, $(C_8H_6N_2)_2,H_2PtCl_6$, which is obtained as a yellowish, crystalline precipitate, decomposes at 280°. The *aurochloride* crystallises in dark yellow needles and melts at 146°. *Cinnoline methiodide*, $C_8H_6N_2,CH_3I$, crystallises in glistening, reddish-brown needles and melts at 168°. J. J. S.

Methylanthranilic Acid and some Quinazoline Derivatives. By G. FORTMANN (*J. pr. Chem.*, 1897, [ii], **55**, 123—136).—Methylanthranilic acid (Zacharias, Abstr., 1891, 912) is best prepared by heating anthranilic acid with caustic potash and methylic iodide. The *copper* salt crystallises with $1H_2O$. *Nitrosomethylanthranilic acid* forms yellowish crystals melting at 128°. The corresponding *hydrazine*, which can only be obtained with difficulty and in small quantity, forms white crystals melting at 120°. *Acetomethylanthranilic acid* is a white, crystalline powder melting at 186°. *Benzomethylanthranilic acid* melts at 161°. Methylanthranilic acid readily reacts with phenylcarbimide, forming 3′ : 1′-*phenylmethyldiketoquinazoline*,

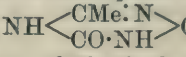


$$C_6H_4{<}\begin{array}{l}CO-NPh\\ NMe\cdot CO\end{array},$$

which crystallises in white needles melting at 233°. It is an indifferent substance, and appears not to yield salts. Ethylcarbimide does not yield a quinazoline derivative with the acid, but complete decomposition occurs when it is heated. Paratolylcarbimide yields 3′ : 1′-*tolylmethyldiketoquinazoline*, which crystallises in slender, white needles melting at 254°. With phenylthiocarbimide, the acid yields 3′ : 1′-*phenylmethylthiodiketoquinazoline*,  $C_6H_4{<}\begin{array}{l}CO-NPh\\ NMe\cdot CS\end{array}$, which melts at 288—289°, and does not yield salts.

1′ : 3′-*Dimethylthiodiketoquinazoline*, obtained by the use of methylthiocarbimide, melts at 186° ; when heated with mercuric oxide and water, it is converted into 1′ : 3′-dimethyldiketoquinazoline, melting at 151° (Abt, Abstr., 1889, 639). The corresponding allyl derivative could not be obtained. Phenylcarbimide unites with acetylanthranilic acid to form an *additive* compound which melts at 175°. The corresponding *benzoyl* derivative melts at 175°. Ethylcarbimide and phenylthiocarbimide, on the other hand, do not appear to combine with acetyl- and benzoyl-anthranilic acids. A. H.

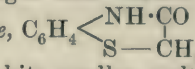
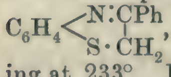
Imidomethyloxytriazine. By ADRIANO OSTROGOVICH (*L'Orosi*, 1896, **19**, 397—402 ; also *Gaz*, **27**, i, 222—228. Compare Abstr., 1896, i, 262).—On heating acetylurethane with guanidine carbonate in a sealed tube for 6 hours at 135—140° and washing the solid product with alcohol, guanidine carbonate is extracted, leaving a residue of *imidomethyloxytriazine carbonate*, $(C_4H_6N_4O)_2,H_2CO_3$, which crystallises in small pyramids and is decomposed by boiling with water.

Imidomethyloxytriazine,  $NH<\begin{matrix}CMe:N\\CO\cdot NH\end{matrix}>C:NH$, is best prepared by treating a boiling solution of the hydrochloride or sulphate with sodium carbonate, when it separates slowly as a white, crystalline powder which, on heating, decomposes without melting. The *hydrochloride*, $C_4H_6N_4O,HCl$, is crystalline and very soluble, whilst the *sulphate*, which crystallises with $3H_2O$ in hard, white prisms, is sparingly soluble in water. The *picrate* blackens at 260°, and is not explosive, whilst the *silver* salt, $C_4H_5N_4OAg$, is a white powder which yields alkylic derivatives when treated with alkylic iodides.

W. J. P.

A New Synthesis of Phenylated Tetrazo-derivatives. By Edgar Wedekind (*Ber.*, 1897, **30**, 449—451).—Nitrous acid reacts with guanazylbenzene on warming, with the formation of a compound identical with the diphenyltetrazole obtained from parahydroxytriphenyltetrazoliumchloride.

The same compound is produced when guanazylbenzene is treated with nitric acid at a moderately high temperature. J. F. T.

Derivatives of Benzoparathiazines [Phenoparathiazines]. By Oskar Unger (*Ber.*, 1897, **30**, 607—610).—When bromacetic acid is brought into contact with amidothiophenol, *ketodihydrophenoparathiazine*,  $C_6H_4<\begin{matrix}NH\cdot CO\\ |\\ S—CH_2\end{matrix}$, is quantitatively formed; this crystallises in long, white needles, melts at 179°, and dissolves in concentrated hydrochloric acid and in aqueous potash. Bromacetic bromide, on the other hand, enters into reaction with two molecules of amidothiophenol, forming the *hydrobromide of a base*, $C_{14}H_{15}N_2OS_2Br$, which melts at 197°. Its alcoholic solution is decomposed by water, the free *base*, $C_{14}H_{14}N_2OS_2$, being precipitated in slender needles melting at 88—89°; the constitution of this substance has not yet been ascertained. With ω-bromacetophenone, amidothiophenol yields *phenylphenoparathiazine*,  $C_6H_4<\begin{matrix}N:CPh\\ |\\ S\cdot CH_2\end{matrix}$, which crystallises in light, sulphur-yellow cubes melting at 233°. It is not affected by acetic anhydride or nitrous acid, but hydriodic acid and phosphorus reduce it to aniline, hydrogen sulphide, and an oil which is probably ethylbenzene. Ethylenic bromide, when heated with amidothiophenol, yields the hydrochloride of the ethylene ether of amidothiophenol; the *base* itself melts at 82°. When the solution of amidothiophenol in ethylenic bromide is heated with hydrochloric acid at 150—160°, the *bromethyl ether*,

$$NH_2\cdot C_6H_4\cdot S\cdot CH_2\cdot CH_2Br,$$

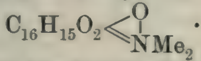
is formed as an oil which volatilises slowly with steam. A. H.

Stearates of the Alkaloids and their Therapeutic Application. By Francesco Zanardi (*Chem. Centr.*, 1896, i, 765; from *Boll. chim. farm.*, 1896, 4).—*Morphine stearate*, $C_{17}H_{19}NO_3,C_{17}H_{35}\cdot COOH$, prepared by slowly adding morphine to an alcoholic solution of stearic acid, forms crystals which can be dried at 30—40°. It is also obtained on mixing aqueous solutions of sodium stearate and morphine hydrochloride, as a voluminous mass which, on recrystallisation from alcohol, forms white, pearly scales melting at 84—86°. It is easily soluble in hot alcohol, slightly so in ether and in cold alcohol, and also in oils to the extent of about 1 per cent., and in fats and vaselin.

Atropine stearate, $C_{17}H_{23}NO_3,C_{17}H_{35}\cdot COOH$, which is prepared in a similar way to the morphine salt and resembles it also as regards solubility, crystallises in white, pearly needles, and melts at 120°. A solution of 0·1 gram in 50 grams of almond oil is a suitable substitute for the oils of henbane and belladonna.

Cocaine stearate, $C_{17}H_{21}NO_4,C_{17}H_{35}\cdot COOH$, is prepared in a similar manner to the preceding salts, and resembles them as regards solubility. It crystallises in white needles, and melts at about 90°.

The presence of stearic acid in these stearates was proved by means of copper sulphate, and the alkaloids were identified by their characteristic reactions. E. W. W.

Morphine Methohydroxide. By EDUARD VONGERICHTEN (*Ber.*, 1897, 30, 354—357).—The loss of water which crystallised morphine methohydroxide, $C_{17}H_{19}NO_3,MeOH + 5H_2O$, has long since been observed to undergo at 100° corresponds best with the formation of an intramolecular anhydride, which would be a hydrogenised phenolbetaine,  $C_{16}H_{15}O_2{<}\begin{matrix}O\\ |\\ NMe_2\end{matrix}$ · Morphine methiodide was converted, by successive treatment with silver sulphate and barium hydroxide, into the methohydroxide, and this was found to unite with methylic iodide in methylic alcoholic solution, yielding codeine methiodide, convertible into methylmorphimethine by boiling with aqueous sodium hydroxide. Codeine methiodide would then have the constitution

$$OMe\cdot C_{16}H_{15}O_2\vdots NMe_2I.$$

It is thought that this view of the relationship of the two substances satisfactorily explains the striking differences observed between the methiodides and methohydroxides of codeine and morphine respectively. C. F. B.

Aconitum Septentrionale (Koelle). By H. V. ROSENDAHL (*J. Pharm.*, 1896, [vi], 4, 262—266).—This plant has yielded the three alkaloids, lapaconitine, septentrionaline and cynoctonine. *Lapaconitine*, $C_{34}H_{48}N_2O_8$, occurs in well-developed crystals, probably hexagonal; it melts at 205°, is soluble in 126 parts of alcohol, 330 parts of ether, or 1472 parts of water; the solutions of the alkaloid and of its salts are dextrogyrate and possess a reddish-violet fluorescence. A *tribromo*-derivative was obtained. When warmed with alkalis, lapaconitine yields an alkaloid melting at 98°, and readily soluble in ether; an alkaloid sparingly soluble in ether, and melting at 106°; and a crystalline acid melting at 114° and free from nitrogen.

Septentrionaline, $C_{31}H_{48}N_2O_9$, which is a yellowish powder melting at 128·9°, acts as an anæsthetic. Its solutions and those of its salts are dextrogyrate and non-fluorescent; it is readily soluble in alcohol and ether, but only moderately so in water. It yields a *tribromo*-derivative, and on warming with alkalis is converted into an alkaloid readily soluble in ether (m. p. 88°); an alkaloid sparingly soluble in ether (m. p. 105°); and the same acid as that obtained from lapaconitine.

Cynoctonine, $C_{36}H_{55}N_2O_{13}$, is an extremely hygroscopic, amorphous alkaloid, and readily decomposes. It is readily soluble in alcohol, moderately in water, and extremely sparingly in ether. It melts at 137°, and its solutions are dextrorotatory but non-fluorescent. With sulphuric acid, it gives a reddish-brown coloration, and if evaporated just to dryness in the presence of fuming nitric acid, it yields a residue, which on treatment with alcoholic potash gives a blood-red coloration. A *tribromo*-derivative has been obtained. The physiological actions of the three alkaloids are given in some detail, and the paper concludes with a summary of the alkaloids obtained from different species of aconite, together with a description of their properties. J. J. S.

Ketones of the Tropine Group, VII. Dibenzylidenetropinone. By RICHARD WILLSTÄTTER (*Ber.*, 1897, **30**, 731—736).—*Dibenzylidenetropinone*, $C_8H_9NO(CHPh)_2$, is formed when benzaldehyde is condensed with tropinone in the presence of hydrochloric acid. It crystallises from absolute alcohol in transparent, yellow prisms melting at 152°; the *hydrochloride* forms glistening, light-yellow prisms and needles melting and decomposing at 270—271°; the *phenylhydrazone* crystallises from alcohol in glistening, pleochromatic needles melting at 193°, and the *methiodide* forms silky needles melting and decomposing at 264—265°. J. F. T.

Synthesis of the Hæmoglobins. By WILHELM PREYER (*Ber.*, 1897, **30**, 190—191).—The author points out that, contrary to the statement of Nencki (*Ber.*, 1896, **29**, 2878), synthesised hæmoglobin has been obtained in crystals (Preyer, *Die Blutkrystalle*, p. 137, Jena, 1871). A. H.

Properties of the Alcohol-soluble Proteid of Wheat and of certain other Cereal Grains. By G. L. TELLER (*Amer. Chem. Journ.*, 1897, **19**, 59—69).—A 1 per cent. salt solution extracts more nitrogenous matter from wheat flour than do stronger solutions (10 per cent. and 15 per cent.), the difference being due to such compounds as are not precipitated from the solution when alcohol is added until it contains 75 per cent. The filtrate from such a solution gives the characteristic proteose reactions, as well as the biuret reaction for proteids.

Careful estimations of the proteids soluble in alcohol extracted from wheat by 1 per cent. salt solution show that, after subtracting the amidic nitrogen, the amount of such proteid present contains 0·27—0·30 per cent. of nitrogen on the wheat taken, and is almost constant in the samples of wheat which were examined; this proteid is probably gliadin. The solubility of this substance indicates another source of inaccuracy in the estimation of the gluten in wheat by washing. It appears that the proteoses which have been found in the aqueous or dilute salt extracts of wheat, barley, oats, and rye are in reality the proteids soluble in alcohol. (Compare Chittenden and Osborne, *Amer. Chem. Journ.*, **13** and **14**). A. H.

Organic Chemistry.

Action of Nickel on Ethylene. By Paul Sabatier and Jean B. Senderens (*Compt. rend.*, 1897, **124**, 616—618).—Nickel reduced from the oxide by hydrogen and allowed to cool in a current of the gas has no action on ethylene at the ordinary temperature, but at about 300°, and still more readily at a somewhat higher temperature, the nickel gradually intumesces and yields a very bulky black product, which is a mixture of nickel and carbon. The reaction is most rapid when the metal has been reduced at a low temperature (about 300°), but it takes place readily even if the metal has been reduced at a red heat. If the layer of reduced metal is about 20 cm. long, the ethylene is completely decomposed, and the issuing gas is a mixture of methane with from 10 to 50 per cent. of hydrogen, according to the temperature at which the reaction takes place, the proportion of hydrogen being higher the higher the temperature. Minute traces of higher hydrocarbons of the methane series also seem to be formed. The main reaction is probably $C_2H_4 = C + CH_4$, the liberation of hydrogen being due to a secondary reaction which takes place under conditions not yet well defined.

A relatively small quantity of nickel will decompose a large quantity of the gas. The reaction can scarcely be attributed to absorption of the ethylene by porous metal, because the decomposition takes place with nickel filings, although less regularly and at a higher temperature. No similar decomposition takes place with finely-divided iron, cobalt, copper, platinum, or palladium, and in this respect the change differs from the decomposition of acetylene as observed by Moissan and Moureu (Abstr., 1896, i, 585). It is possible that an unstable compound of nickel and ethylene is first formed and afterwards splits up into nickel, carbon, and methane.

Ethylene acts on nickel oxide at a comparatively low temperature, and the phenomena will be described subsequently. C. H. B.

Decomposition of Hexane and Trimethylethylene by Heat. By Fritz Haber (*Chem. Centr.*, 1896, ii, 237—240; 377; from *J. Gasbel*, **34**, 377—382, 395—399, 435—438, 452—455).—From his researches on acetylene, Berthelot regarded the reactions occurring in the flame as consisting of decomposition of hydrocarbons with liberation of hydrogen, recombination of these products, and union of simpler hydrocarbons to form denser ones. Between these processes of decomposition and combination, a complicated state of equilibrium was supposed to be established. To these views the author raises the following objections. It is entirely unproved that all the hydrocarbons result from the repeated splitting off of hydrogen and condensation of the residues. At high temperatures, direct decomposition into carbon and hydrogen, with immediate polymerisation of the atoms of the former, may also occur. The theory of equilibrium is only based on a qualitative proof of a series of hydrogen-additions and hydrogen-eliminations in the case of some simple hydrocarbons (acetylene, ethylene, methane, and amylene), and the enormous number of compounds which should result according to this theory have never been observed. The importance of acetylene in this series of equilibria is not intelligible, since, according to Berthelot's experiments, it is only present in very limited quantity, and, moreover, it readily forms aromatic compounds, whilst on heating with hydrogen, ethylene is produced in very variable quantity according to the conditions, and on heating with ethylene, it only yields some crotonylene.

In opposition to Lewes' theory of the luminosity of flame (Trans., 1892, 322), the author points out that tarry substances, formed by the polymerisation of decomposition products, are found, not only in the luminous, but also in the non-luminous zone of the flame, and as long as it is not proved that these tarry substances decompose into acetylene before being resolved into carbon and hydrogen, Lewes' theory of the luminosity being caused exclusively by the decomposition of acetylene is untenable (compare A. Smithells, Trans., 1892, 204). Haber has chosen normal hexane for experiment for the following reasons: (1) Because it is susceptible of decomposition into lower hydrocarbons, for example, $C_6H_{14} = C_5H_{10} + CH_4$, in a way which is impossible in the case of simpler hydrocarbons, such as methane, ethane, &c.; (2) because it can be partially decomposed by exposure for a short time to an incipient red heat, whilst the lower hydrocarbons require a high temperature, which renders it impossible to isolate the products of decomposition in their primary form; (3) because a direct conversion into aromatic compounds, as suggested by Armstrong and Miller, in the case of higher aliphatic compounds, could especially easily take place in the case of this six-carbon hydrocarbon; (4) because hexane being the chief component of commercial gasoline, a knowledge of its decomposition products is of great importance.

The experiments showed that hexane and trimethylethylene decompose into smaller molecules without liberation of hydrogen. In the aliphatic series, the union of carbon and hydrogen atoms is stronger than that of carbon with carbon, whilst in the aromatic series the reverse is the case, hence the stability of benzene and solid hydrocarbons containing one or two carbon atoms as compared with the ready decomposition of the higher aliphatic compounds; in this connection, the author quotes the researches of Breitenlohner, Vohl, Thorpe and Young. A second regularity was shown in the fact that by superheating the vapours of hydrocarbons at a high temperature for a short time, a portion was simply split off from the end of the carbon chain with some rearrangement of the hydrogen atoms in such a way that the larger residue always contained a double bond when the original hydrocarbon possessed none. Apparently, hydrocarbons with less than three carbon atoms are split off, and it depends on the conditions as to whether these are methane, ethane, ethylene, or acetylene. The reaction lying at the basis of this decomposition is shown by heating hexane for about two seconds to 600—800°, when very little formation of hydrogen takes place, and the addition of hydrogen to the olefines is also insignificant, because at this temperature the union of hydrogen, even with acetylene, is very slow. Trimethylethylene behaves very similarly to hexane, but the heavier product of decomposition unites with other molecules to form more complex hydrocarbons.

There is no equilibrium established between the reactions of decomposition and recombination, but the latter are of an altogether different character to the former. Between 900° and 1000°, secondary reactions become more evident, and even in the case of hexane, at this temperature the primary decomposition products are not all stable. By continued splitting off of terminal portions of the chain, more complex tarry substances are formed and hydrogen is liberated in noticeable amount, the decomposition of the lowest members of the different series (Berthelot and Lewes' special case) beginning to take place alongside the decomposition of the original material. At this point, the liberated gases contain hydrogen, methane, ethylene, benzene, and traces of other hydrocarbons. From a mathematical examination of the analytical results, the author infers that a portion of the products of decomposition at lower temperatures which has been held to contain homologues of methane, consists in reality of compounds containing less hydrogen, very similar to the paraffin group and possibly belonging to the trimethylene series. Direct formation of benzene from hexane was not proved, and the fact that both hexane and trimethylethylene give the same yield of benzene, indicates that this hydrocarbon is formed exclusively from acetylene. From a comparison of the weights of gaseous olefines and benzene obtained in the various decompositions, it is seen that, at a dark red heat, the carburation value of the products depends essentially on the olefines. At 900—1000°, on the other hand, the carburation value is only half, owing to the greater quantity of benzene. In practice, the conditions for the formation of benzene are more unfavourable, but in spite of this, the gas from gasoline at a high temperature showed that a certain proportion of the carburation value was to be ascribed to benzene. At 900—1000°, benzene becomes unstable, and hence its formation from hexane and trimethylethylene decreases.

[With H. SAMOYLOWICZ].—*Decomposition of Hexane.*—Details are given of the methods employed in analysing the products of the decomposition.

In order to ensure that the gas was uniformly heated throughout, coils of narrow glass combustion tubing were used, being heated in baths of sulphur (448°), phosphorus pentasulphide (518°) or stannous chloride (606°). When zinc chloride was used, a brass coil was employed. This was freely suspended in a steel crucible round which a second steel crucible was fitted, the space between containing the chloride. The inner crucible was closed by a porcelain lid through a hole in which the ends of the coil, protected by means of a porcelain tube, passed. For heating purposes, a small muffle or an asbestos fire-clay furnace was used. In some cases, air baths consisting of iron crucibles with fitted conical tops were employed, the coil wrapped in asbestos being suspended in the lower vessel and the temperature ascertained by means of the Prinsep's alloy contained in the asbestos covering. The vaporisation of the hexane was effected by slowly admitting the liquid into a flask heated at 100° to which a delivery tube leading to the decomposition coil was attached. The coil was connected successively with a condenser and a distilling flask, both immersed in a mixture of ice and salt, the latter serving as a reservoir for the collection of tar, then came a Winkler's coil cooled by ice, a second coil for condensation of paraffin oils, and finally the gas reservoir, a vessel of 69 litres capacity with a stopper fitted with thermometer, gas-delivery tube, water exit pipe, and manometer. The flow of water was regulated by varying the length of the longer arm of the siphon.

Hexane remains unchanged if heated for a short time at 518°, but at 606° the decomposition is very considerable, olefines and paraffins being the main products with some hydrogen and benzene, which is indicative of rupture of the carbon chain in such a way that, from one molecule of hexane, one molecule of an olefine and one of a paraffin are formed. Of the paraffins, methane is the most abundant, constituting at least 70 per cent., hence the decomposition consists essentially in the splitting off of a terminal CH_3 group with formation of amylene and methane. The small amount of liquid olefines in comparison with the gaseous olefines and the mean molecular weight of the latter, namely 39, indicate that amylene undergoes a secondary decomposition to some extent into ethylene and propylene. Acetylene, hydrogen, and carbon result from an insignificant bye-reaction whose nature was not determined. Two experiments at 730° and 820° showed a similar decomposition. In one experiment, direct proof of the presence of propylene, amylene, and ethylene was obtained by employing a coil containing fuming sulphuric acid, which absorbs the two former with ease and the last only with difficulty. In all these experiments, the separation of carbon was extremely small, but at temperatures from 1190—1220° the separation was so great that the cast iron heating tubes of 10 mm. bore were soon choked. The greater portion of the hexane was decomposed into its elements and there was no condensation of tar. Besides hydrogen (65·2 per cent.) the only hydrocarbon found in considerable quantity (22·6 per cent.) was methane, acetylene occurring only in traces.

The gases obtained at temperatures up to 820° were photometrically examined. Hexane was found to be one of the best materials for the production of oil gas. This substance furnishes a gas which, "after cooling to – 10° and washing with paraffin oil at 0°, possesses a candle power of 61·5—74·5 English candles per consumption of 5 cubic feet and of 186·5—198 candles per kilogram of original material." Tar consisting of a mixture of unchanged hexane and amylene is also produced to the extent of 37—48 per cent. The value of hexane and similar materials for the production of gas has been hitherto far underestimated, as they have been tried under unfavourable conditions, producing a gas containing only 30 per cent. of olefines instead of, as in this case, 50 per cent. E. W. W.

Derivatives of Diamylene and of Isodibutylene. By IWAN ROBERT SCHINDELMEISER (*Chem. Centr.*, 1896, ii, 354; from *Diss. Dorpat*, 1896).—Halogen compounds were prepared from both hydrocarbons, and alcohols possessing a peculiar, putrid, musty odour were obtained from the iodides. On decomposition with alcoholic potassium hydroxide, diamylenic chloride re-forms diamylene, whilst isodibutylene chloride gives, not only isobutylene, but also a hydrocarbon, which results probably from the displacement of the hydroxyl group by chlorine, and which has an odour similar to that of isodibutol.

E. W. W.

Action of Acetylene on Cupric Salts. By HENRIK G. SÖDERBAUM (*Ber.*, 1897, **30**, 760—765).—The action of acetylene on cupric salts seems to have been for the most part disregarded, although on passing a stream of the pure gas into an ammoniacal solution of either cupric sulphate or nitrate, a black, flocculent precipitate is slowly produced.

This substance, after being dried over sulphuric acid, gave various results on analysis, a fact which was found to be due to the absorption of oxygen from the air during the process of drying; in an exhausted desiccator, however, the substance ceased to increase in weight after 2 days, and then yielded, on analysis, numbers corresponding with the formula $(C_{17}Cu_8H_4O_3)_n$. This *copper acetylide* is a black, amorphous powder insoluble in water and organic solvents; it explodes between 70° and 80° when heated, and decomposes quickly on heating with hydrogen chloride with formation of the halogen salt of copper, and a carbonaceous residue of the formula $(C_{12}H_4O_3)_n$; this is probably similar to the graphite hydrate obtained by Schützenberger and Bourgeois from crude iron.

On passing acetylene into a neutral or faintly acid solution of copper acetate, a precipitate is formed corresponding in composition with the formula $(C_8Cu_4O)_m + (H_2O)_n$, and differing from the compound above mentioned in being stable in the air and non-explosive. It seems, therefore, from these experiments, that a large number of copper acetylides are capable of existing.

J. F. T.

Action of Acetylene on Cupric Salts. By HENRIK G. SÖDERBAUM (*Ber.*, 1897, **30**, 814—815).—The composition of the precipitate produced by acetylene in a dilute ammoniacal solution of copper sulphate varies with the temperature at which the precipitation is effected. At +5°, the compound, after drying over phosphoric anhydride, has the composition $C_{24}H_2Cu_{12}O$ ($= 12C_2Cu + H_2O$), and is a black powder, which explodes at 50° when quickly heated, and is dissolved by potassium cyanide and dilute sulphuric and hydrochloric acids, a small amount of a carbonaceous residue being invariably left. At 15°, the acetylide contains less copper, whilst the amount of carbon remains practically unaltered. The atomic ratio of carbon to copper, therefore, is at this temperature greater than 2 : 1.

A. H.

Magnesium Methoxide. By EMERICH SZARVASY (*Ber.*, 1897, **30**, 806—809).—*Magnesium methoxide*, $Mg(OMe)_2$, is formed when perfectly bright magnesium ribbon is placed in absolute methylic alcohol at the ordinary temperature and when the two are heated together; if the solution thus formed contains about 6 grams of magnesium to 40 grams of methylic alcohol, transparent, pointed prisms are deposited, which contain 3 mols. methylic alcohol, effloresce rapidly in the air, and are soluble in ethylic alcohol and in benzene. From more concentrated solutions, the methoxide separates as an amorphous mass and is deposited as an amorphous powder when its solutions are heated. When treated with water, it yields magnesium hydroxide and methylic alcohol, and when heated in a vacuum, it decomposes, evolving a mixture of carbonic anhydride, carbonic oxide, and hydrogen. Bromine converts it into bromoform and magnesium bromide. A. H.

Reaction of Mercaptides with Alkylic Iodides.—By KARL A. HOFMANN and W. O. RABE (*Zeit. anorg. Chem.*, 1897, **14**, 293—296).—Hydrogen platinochloride, when treated with ethylic mercaptan in alcoholic solution, yields platinic mercaptide, $Pt(SEt)_4$, which, when allowed to remain in a vacuum at 100°, is quickly converted into platinous mercaptide. The latter, when heated with ethylic iodide in a pressure flask for 2 days at 70° to 80°, yields the compound $Pt(Et_2S)_2I_2$, which separates in large, red crystals, melts at 137°, and is identical with Blomstrand's platosoethylsulphine iodide obtained from platinum iodide and ethylic sulphide. Methylic iodide reacts with platinous mercaptide more quickly than ethylic iodide, and yields the compound $Pt(SEtMe)_2I_2$ which melts at 98°; this, when treated with silver nitrate in alcoholic solution yields all its iodine as silver iodide at the ordinary temperature.

Palladium chloride and ethylic sulphide yield the compound $Pd(SEt)_2$. Iridium sesquichloride yields the compound $Ir(SEt)_2$.

Mercury mercaptide when treated with ethylic iodide for 24 hours at the ordinary temperature, and then at 40° to 50°, yields the double compound HgI_2,SEt_3I; this crystallises in yellow needles, melts at 107°, and when treated with hydrogen sulphide in alcoholic solution is decomposed into red cinnabar and triethylsulphine iodide. The corresponding methyl compound, HgI_2,SMe_3I, crystallises in large, yellow plates, melts at 160°, and when treated with dilute nitric acid yields free iodine, and after prolonged boiling, mercury iodide. E. C. R.

Allylic Phosphates. By JACQUES CAVALIER (*Compt. rend.*, 1897, **124**, 91—92).—In a former communication (Abstr., 1895, i, 638), the preparation of allylphosphoric acid, $C_3H_5H_2PO_4$, by the action of phosphoric anhydride on allylic alcohol in ethereal solution was described. The mother liquors from the barium salt of this acid yield, on evaporation, the barium salt of diallylphosphoric acid, $(C_3H_5)_2HPO_4$, as a gelatinous mass. This can be converted into the *lead* salt, $[(C_3H_5)_2PO_4]_2Pb$, crystallising in fine, colourless needles. *Triallylic phosphate*, $(C_3H_5)_3PO_4$, is prepared by the action of triargentic phosphate on allylic iodide, but is difficult to purify. When boiled with barium hydroxide and water, it yields barium diallylphosphate. Diallylphosphoric acid is stable in aqueous solution in the cold, but when warmed it yields first allylphosphoric acid and then phosphoric acid. The diallylphosphates are much more stable in solution than the acid itself. The sodium and potassium salts are deliquescent, and crystallise with difficulty; the salts of calcium, barium, lead, and silver crystallise without water and are very soluble. Lead diallylphosphate melts at 151°, and when heated to 200° decomposes into triallylic phosphate which vaporises, and lead allylic phosphate which burns at a higher temperature, lead pyrophosphate alone remaining. The silver salt behaves in a similar manner.

When the calcium salt is heated to a high temperature, it decomposes, leaving a residue of calcium metaphosphate. A. C. C.

Separation of Galactose and Arabinose. By EUNM SUBASCHOW (*Chem. Centr.*, 1896, ii, 134—135; from *Zeit. Ver. Rübenzuck-Ind.*, 1896, 270—273).—*Galactosebenzhydrazide*, $C_{13}H_{18}N_2O_6,H_2O$, is prepared by digesting a mixture of 1 part of galactose with the calculated quantity of benzhydrazide and 20—25 parts of 96 per cent. alcohol on the water bath. After 1½—2 hours, the whole mass is liquid, and on cooling some galactosebenzhydrazide separates out, but the main portion only after evaporating down to one-third or one-fourth. After crystallisation from alcohol, this compound forms long, white, rectangular plates, melts at 78° becoming brown, and is slightly soluble in cold water, easily in hot water with partial decomposition, very soluble in hot 96 per cent. alcohol, and slightly so in the cold.

Arabinosebenzhydrazide is prepared in a similar way; the arabinose dissolves almost instantaneously, and in 15—20 minutes the hydrazide, $C_{12}H_{16}N_2O_5$, begins to separate, and after boiling half-an-hour and cooling is completely deposited. After crystallisation from alcohol, it forms white, silky plates, melts and decomposes at 184°, and is very slightly soluble in cold water, easily in hot, with partial decomposition, almost insoluble in çold 96 per cent. alcohol, very slightly soluble on boiling, and more easily so in dilute hot alcohol. Arabinosebenzhydrazide may also be prepared by digesting cherry-gum with dilute sulphuric acid and subsequently treating with benzhydrazide. With benzaldehyde in alcoholic solution, it forms benzylidenebenzhydrazide.

The separation of arabinose from galactose depends on the different rates of formation of their benzhydrazides and their different solubilities. For example, 200 grams of gum arabic, a sample of which, on oxidation with nitric acid, gave a large quantity of mucic acid, was digested with 400 grams of 6 per cent. hydrochloric acid on the water bath for 6 hours. After neutralisation with lead carbonate and decolorisation with bone charcoal, the filtrate was evaporated to 75 c.c., when it yielded a syrup of density 1·168, which was treated with 10 grams of benzhydrazide and 75 grams of water. After remaining a day at the ordinary temperature, a precipitate was formed which, when purified, melted at 184°. E. W. W.

Carbohydrates in Beer. By PAUL PETIT (*Compt. rend.*, 1897, 124, 510—511).—Beer that has been kept in a cool place for 3 months contains half of its extractive matter in the form of dextrin, containing about 3·6 per cent. of pentoses. Its rotatory power is $a_D = 149·6°$, and its reducing power 13·4 per cent. in terms of maltose, and 6·3 per cent. in terms of glucose. In several ways, it behaves differently from ordinary dextrin; it is less readily inverted by hydrochloric acid, but the hydrolysis proceeds further, and is not limited by the formation of dextrose; it is also less readily converted into brown products by the prolonged action of the acid.

When heated with diastase for an hour at 52°, with yeast for 3 days at 27°, and with a mixture of diastase and yeast for 3 days at 27°, the beer dextrin yields the following results:

	Rotatory Power.	Reducing Power. (Maltose.)
Initial	149·6°	13·4
With diastase	125·3	18·7
With yeast	106·5	10·5
With yeast and diastase	32·1	4·7

It is noteworthy that, after the combined action of yeast and diastase, and after the action of hydrochloric acid for 3 hours, the products from the beer dextrin have practically the same rotatory powers, whilst the rotatory power after fermentation with yeast alone is practically identical with that observed after the action of hydrochloric acid for an hour and a quarter, the latter being the time required for the conversion of ordinary dextrin into dextrose under the same conditions. C. H. B.

Action of Iodine on Starch. By Gaston Rouvier (*Compt. rend.*, 1897, **124**, 565—566).—If it is supposed that, in the action of iodine on starch when the former is in excess, but not in sufficient quantity to form the compound $(C_6H_{10}O_5)_{16}I_5$ (Abstr., 1894, i, 353), the compounds $(C_6H_{10}O_5)_{16}I_3$ and $(C_6H_{10}O_5)_{16}I_4$ are formed and have the power of dissolving a further quantity of iodine, it seems probable that the proportion of iodine dissolved by one or other of them will depend on the concentration of the iodine in the supernatant liquid in accordance with the law of Berthelot and Jungfleisch concerning the partition of a soluble substance between two non-miscible solvents. This view is confirmed by a close agreement between the observed and calculated numbers. C. H. B.

A Third Diastase-Achroodextrin and the Isomaltoses. By Eugen Prior (*Chem. Centr.*, 1896, ii, 86; from *Centr. Bakt. Parasitenk*, **2**, [Abtlg. II], 271—273).—The author has examined the products obtained by the incomplete saccharification of potato starch by green malt according to the method of Lintner and Düll. From the mixture, which still shows the erythrodextrin reaction, the easily fermentible sugars and the greater portion of the maltose were removed by fermentation with Saaz yeast. The residue, which must contain Bau's β-isomaltose, when treated with alcohol of various strengths and fermented a second time, yielded the third dextrin, which has approximately a rotatory power of 173° and a cupric-reducing power of 53·7 (maltose = 100). This dextrin is distinguished from achroodextrin I and II by its fermenting with difficulty with the Frohberg and Saaz yeasts, being attacked by the former more than by the latter under the ordinary conditions at 25°, but it is completely decomposed by both in the author's vacuum apparatus. By mixing this dextrin with about 20 per cent. of pure maltose and treating the product with phenylhydrazine acetate, no trace of maltosazone could be obtained, but the osazone of melting point 150—152° which has been hitherto regarded as the characteristic isomaltosazone is formed. The mixture of dextrins obtained from the residue after fermentation and insoluble in 80 per cent. alcohol, behaves similarly when mixed with maltose. The author therefore regards the isomaltoses principally as mixtures of achroodextrin III and maltose, but is yet uncertain as to whether the former is identical with Lintner and

Düll's achroodextrin, $(C_{12}H_{20}O_{10})_2 + H_2O$, which is theoretically possible but has not yet been prepared. The author is engaged on the purification and examination of an achroodextrin of lower rotatory power and higher reducing properties, obtained by the action of diastase on starch. E. W. W.

Electrolytic Conversion of Nitriles into Amines. By FELIX B. AHRENS (*Zeit. Elektrochem.*, 1896, **3**, 99).—The author finds that nitriles are reduced to amines when solutions of them, which may be acid or alkaline, are placed in the cathode compartment of an electrolytic cell; hydrolysis of the nitrile takes place simultaneously, diminishing the yield of amine obtained, this being especially the case with alkaline solutions. Acetonitrile dissolved in 5 per cent. sulphuric acid gave ammonia alone, whilst with 3 per cent. acid, some ethylamine was obtained; propionitrile, in acid solution, gave considerable quantities of normal propylamine, whilst benzonitrile gave only benzylamine. Phenylethylamine was also obtained from benzylic cyanide. Alkaline solutions gave less favourable results. T. E.

Dibromodiethylamine. By SIEGMUND GABRIEL and GEORG ESCHENBACH (*Ber.*, 1897, **30**, 809—813).—Diphenoxydiethylamine, $NH(C_2H_4 \cdot OPh)_2$ (Weddige, Abstr., 1881, 1136), readily reacts with hydrobromic acid at 150° forming *dibromodiethylamine hydrobromide*, $NH(C_2H_4Br)_2,HBr$, which crystallises in colourless scales, and melts at 199—200°. The *picrate* melts at 128°, and the *bismuthoiodide* at 164—165°, whilst the *platinochloride* melts and decomposes at 222°. The bromine atoms cannot readily be removed by the action of aqueous potash, but when the hydrobromide is digested with aqueous silver nitrate, it is converted into *dihydroxydiethylamine nitrate*,

$$NH(C_2H_4 \cdot OH)_2,HNO_3,$$

which crystallises in colourless, pointed rhombs and melts at 69°. The *aurochloride* melts at 119—120°, and the platinochloride, which was first prepared by Wurtz (*Annalen*, 1862, **121**, 227), melts and decomposes at 160—161°. A. H.

Amidoethylic Alcohol (1 : 2-Ethanolamine). By LUDWIG KNORR (*Ber.*, 1897, **30**, 909—915).—Amidoethylic alcohol, or hydroxyethylamine, is best prepared by the action of ammonia on ethylenic oxide (Wurtz), dihydroxydiethylamine and trihydroxytriethylamine being also produced, in relative quantities which depend on the concentration of the ammonia employed. The three bases can then be separated without difficulty by fractional distillation. The same bases are formed by the action of ammonia on ethylene chlorohydrin, but they cannot be so easily isolated. Hydroxyethylamine is a thick, colourless oil with a faint odour resembling that of ethylenediamine. It boils at 171°, has a sp. gr. = 1·022 at 20°, the molecular refraction 16·17, and the molecular dispersion 0·50. It dissolves in about 100 parts of ether, and is more readily volatile with ether vapour than with steam. The base fumes in the air, and its vapour destroys cork, whilst its solution in water, with which it is miscible in all proportions, acts on the skin like a strong alkali. The *aurochloride* crystallises in long needles melting at about 190°. It forms a very characteristic salt with 1′-paranitrophenyl-3′-methyl-4′-nitro-5′-pyrazolone, which the author proposes to term *picrolonic acid*. *Hydroxyethylamine picrolonate*, $C_2H_7NO,C_{10}H_8N_4O_5$, is sparingly soluble in water and alcohol, and crystallises in fascicular groups of yellow needles, which melt and decompose at about 225° when rapidly heated, at about 220° when slowly heated. The *dibenzoyl* derivative crystallises in thin plates melting at 76°. A. H.

Diethanolamine [Dihydroxydiethylamine]. By LUDWIG KNORR (*Ber.*, 1897, **30**, 915—918. Compare the foregoing abstract).—*Dihydroxydiethylamine*, $NH(CH_2\cdot CH_2\cdot OH)_2$, crystallises in fibrous masses melting at 28°; it boils at 270° (pressure = 748 mm.) and at 217—218° (pressure = 150 mm.), has a sp. gr. = 1·0966 at 20°, the molecular refraction 27·08, and the molecular dispersion 0·880. It is hygroscopic, and resembles monhydroxyethylamine in its other properties, but is not volatile with steam. The *aurochloride* crystallises in long needles melting at about 122°; the readily soluble *picrate* melts at 109—110°, the *picrolonate* at about 216°. The *tribenzoyl* derivative could not be obtained in the crystalline state.

When the free base is heated at 160° with 70 per cent. sulphuric acid, it is converted into morpholine, which can thus be obtained in a purer condition than by any other method. A. H.

Triethanolamine [Trihydroxytriethylamine]. By LUDWIG KNORR (*Ber.*, 1897, **30**, 918—921. Compare the two foregoing abstracts).—Trihydroxytriethylamine, $N(CH_2\cdot CH_2\cdot OH)_3$, was prepared in the free state by Wurtz. It boils at 277—279° (pressure = 150 mm.), has sp. gr. = 1·1242 at 20°, the molecular refraction 37·75, and the molecular dispersion 1·274. When caustic potash is added to its aqueous solution, a potassium salt separates in slender needles. The hydrochloride, which melts at 177°, is only sparingly soluble in water, and is insoluble in cold alcohol. The *platinochloride* melts at 118—119°, the *aurochloride* crystallises in four-sided plates containing $1H_2O$, and melts, after being dried, at 77—78°. The *picrate* melts at 126—127°, and is only sparingly soluble in alcohol and water. The *tribenzoate* is a viscid syrup. A. H.

Action of Free Bases on Salts. By ALBERT COLSON (*Compt. rend.*, 1897, **124**, 502—504).—When di-isobutylamine hydrochloride is brought in contact with dry ammonia gas, the latter is rapidly absorbed. The dissociation pressure is 40 mm. at 0°, 53 mm. at 11°, and 85 mm. at 35°. On the other hand, ammonia gas has no action on piperidine hydrochloride, even under a pressure of 775 mm., but piperidine decomposes ammonium chloride, the dissociation pressure exceeding 1 atmosphere at the ordinary temperature, whilst at 0° it is 759—762 mm.

The decomposition of either hydrochloride by ammonia develops heat, and this development is a condition necessary to the results described. Direct experiment shows that, in both cases, there is actual displacement of the base. The decomposition of ammonium salts by the bases is a phenomenon of heterogeneous dissociation, comparable with the action of sulphuric acid on lead chloride (this vol., ii, 211).

Di-isobutylamine and piperidine form no basic hydrochlorides, but when their hydrochlorides are brought in contact with hydrogen chloride, the latter is immediately absorbed, and the dissociation pressures of the compounds formed depend only on the temperature. With di-isobutylamine hydrochloride, this pressure is 195 mm. at 0°, 253 mm. at 7·3°, and 760 mm. at 34°; with piperidine hydrochloride it is 355 mm. at 0°, and 462 mm. at 7·3°. C. H. B.

Preparation of Higher Amines of the Fatty Series: Pentadecylamine. By ELIZABETH JEFFREYS (*Ber.*, 1897, **30**, 898—901).—Hofmann's method for the preparation of fatty amines, does not apply to those high in the series, the yield apparently decreasing as the series advances; by slightly modified methods, such as starting with the acid bromamide, the middle members, for instance, octylamine, have been synthesized in yields of about 45 per cent., and since Lengfeld and Stieglitz have lately shown that acid bromamides in methylic alcohol solution undergo the Beckmann rearrangement with sodium methoxide, forming the urethane derivative of the amine, it seemed interesting to ascertain whether this method could be employed as a means of preparing the higher fatty amines; such was, in fact, found to be the case.

The *chloramide of palmitic acid*, $C_{15}H_{31}\cdot CO\cdot NHCl$, a compound melting at 70—71°, passes almost quantitatively, on treatment with sodium methoxide in methylic alcohol solution, into *pentadecylmethylurethane* (methylic *n*-pentadecylcarbamate), $C_{15}H_{31}\cdot NH\cdot COOMe$, a vitreous, crystalline mass melting at 61—62°; this compound, on hydrolysis with concentrated hydrochloric acid, or distillation with lime, yields *pentadecylamine*, $C_{15}H_{31}NH_2$, a colourless, crystalline substance melting at 36·5° and boiling at 298—301° (uncorr.), the yield of the amine being about 90 per cent. of the theoretical. It was subsequently found that the acid amide itself readily yielded the urethane derivative on treatment with sodium methoxide. It is, therefore, unnecessary to prepare the chloramide. *Pentadecylamine hydrochloride* forms a white, vitreous mass scarcely soluble in water, and yields a *platinochloride*, $(C_{15}H_{31}NH_2)_2,H_2PtCl_6$.

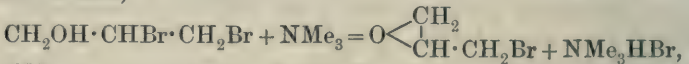
Pentadecylcarbamide, $C_{13}H_{31}\cdot NH\cdot CO\cdot NH_2$, is formed by the action of potassium cyanate on the hydrochloride; it melts at 109°. *Benzoylpentadecylamine* melts at 78°. J. F. T.

Action of Trimethylamine and Pyridine on Chlorhydrins. By HILDERICH HARTMANN (*Chem. Centr.*, 1896, i, 999—1000; from *Diss. Marburg*, 1896, 1—56).—According to V. Meyer and to Scholten, trimethyldihydroxypropylammonium chloride is formed by the action of trimethylamine on α-monochlorhydrin; its platinochloride melts at 230° (Scholten 220°), and its aurochloride at 155° (Scholten 190°). Unlike Scholten, the author finds that acetic chloride reacts only incompletely with the ammonium chloride at 160°, but by heating with acetic anhydride and sodium acetate, the *diacetoxypropyl* derivative is produced; this gives a *platinochloride* melting at 235—236°. Similarly, with benzoic chloride the action is incomplete, but benzoic anhydride at 150—160° forms the analogous *dibenzoyl* derivative; the *platinochloride* melts at 191°. By the action of hydriodic acid at 100° on trimethyldihydroxypropylammonium chloride, the author has obtained two compounds, $C_3H_5I_2\cdot NMe_3I$, which Scholten obtained only at a higher temperature, and $CH_2I\cdot CH(OH)\cdot CH_2\cdot NMe_3Cl$. The latter forms an *aurochloride* melting at 101°, and a *platinochloride* which blackens at 176° and decomposes completely at 194°. By the action of nitric acid on trimethyldihydroxypropylammonium platinochloride, trimethylamine and a new compound, whose analysis shows a composition nearer that of homohydroxybetaine than of homohydroxymuscarine are formed. With platinic chloride, this substance gives a compound, $[COOH\cdot CH(OH)\cdot CH_2\cdot NMe_3]_2PtCl_6$, melting at 233°, and with gold chloride a compound melting at 168—172°. Both salts were analysed. The fact that a copper salt may also be formed indicates the presence of a carboxyl group. In accordance with Niemilovicz's observation, but not with Scholten's, two products are obtained by the action of trimethylamine on α-dichlorhydrin, namely, hexamethylhydroxypropylenediammonium chloride, the platinochloride of which melts at 266° and the aurochloride decomposes at 246°, and trimethylchlorhydroxypropylammonium chloride which gives a platinochloride melting at 168° and an aurochloride melting at 163°. The latter compound is identical with that of the same name obtained by Partheil (Abstr., 1892, 950) in a different way. Its constitution

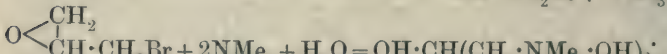
$$CH_2Cl\cdot CH(OH)\cdot CH_2\cdot NMe_3Cl$$

is proved by the above synthesis.

By the action of trimethylamine on β-dibromhydrin, an epibromhydrin is first formed,



$$CH_2OH\cdot CHBr\cdot CH_2Br + NMe_3 = O\Big<\begin{array}{l}CH_2\\ \vert\\ CH\cdot CH_2Br + NMe_3HBr,\end{array}$$



$$O\Big<\begin{array}{l}CH_2\\ \vert\\ CH\cdot CH_2Br + 2NMe_3 + H_2O = OH\cdot CH(CH_2\cdot NMe_3\cdot OH)_2.\end{array}$$

These intermediate products were not isolated, but hexamethylhydroxypropylenediammonium chloride was obtained by means of silver chloride and hydrochloric acid. Trimethylamine acts on β-dichlorhydrin in a manner analogous to the above.

By the action of trimethylamine on allylic tribromide, the author, like Scholten, only obtained a trimethylbromallylammonium chloride, which is identical with the compound obtained by Partheil (*loc. cit.*).

By the action of trimethylamine on epichlorhydrin, hexamethylhydroxypropylenediammonium chloride was obtained, as Scholten found, and from the mother liquor the epi-compound identical with Partheil's anhydrobromoisomuscarine.

By the action of pyridine on β-dichlorhydrin, an additive product appears to be formed which easily decomposes.

Pyridine reacts with epichlorhydrin to form two compounds, the aurochlorides of which, (I) and (II), melt respectively at 235° and 146°.

I. $AuCl_3\cdot C_5H_5\cdot NCl\cdot CH_2\cdot CHOH\cdot CH_2\cdot N(CCl)\cdot C_5H_5\cdot AuCl_3$.

II. $AuCl_3\cdot CH_2Cl\cdot CHOH\cdot CH_2\cdot N(CO)\cdot C_5H_5$. E. W. W.

Condensation of Acetone on Boiling with Excess of Zinc Chloride. By P. N. Raikow (*Ber.*, 1897, 30, 905—906).—On boiling acetone with excess of zinc chloride for many hours, an oily layer gradually separates, becoming thicker as the boiling is prolonged. The product, which evidently contained many substances, was fractionated, and the fractions boiling at 161—162° and 251—252° analysed; the numbers obtained corresponded better with those for terpene than those for mesitylene. J. F. T.

Conversion of Ketones into α-Diketones. II. By MICHELE FILETI and GIACOMO PONZIO (*J. pr. Chem.*, 1897, [ii], **55**, 186—201. Compare Abstr., 1895, i, **15**, 499).—The authors have extended their investigations on the oxidation of ketones by nitric acid to ketones of the type $R\cdot CH_2\cdot CO\cdot CH_2R'$. Diethyl and dipropyl ketones, as might be expected from their symmetrical structure ($R = R'$), yield only one diketone each, $R\cdot CO\cdot CO\cdot CH_2R$, and one dinitrohydrocarbon, $R\cdot CH(NO_2)_2$. Ethyl isopropyl ketone yields only one diketone, in harmony with the fact that it contains only one CH_2 group adjoining the CO group; further, it yields only one dinitrohydrocarbon, dinitroethane. Ethyl propyl ketone yields the two possible diketones, $R\cdot CO\cdot CO\cdot CH_2\cdot R'$ and $R\cdot CH_2\cdot CO\cdot CO\cdot R'$, and the two possible dinitroethanes, $R\cdot CH(NO_2)_2$ and $(NO_2)_2CH\cdot R'$. From ethyl isobutyl ketone, only the diketone $CH_3\cdot CO\cdot CO\cdot CH_2Pr^{\beta}$ could be identified with certainty, and only dinitroethane. It may thus be asserted that the dinitro-derivative obtained is always derived from the alcohol radicle to which belongs the methylene group that is converted into carbonyl. Lastly, among the products obtained from ethyl isopropyl and ethyl isobutyl ketones were substances of the type $CH_3\cdot C(NO_2)_2\cdot CO\cdot R'$; these are unstable, being hydrolysed slowly by dilute acids and water, more quickly by alkalis, into dinitroethane, $CH_3\cdot CH(NO_2)_2$, and acids, $OH\cdot CO\cdot R'$. Palmitone yields neither diketone nor dinitrohydrocarbon.

Propionylbutyryl, $COEt\cdot COPr^{\alpha}$, from dipropylketone, is an oil, lighter than water, and sparingly soluble in it; the *dioxime* melts at 167—168°, the *osazone* at 106°. *Dipropionyl*, $COPr^{\alpha}\cdot COPr^{\alpha}$, from ethyl propyl ketone, was only obtained mixed with acetylbutyryl; its *osazone* melts at 160—161°, the impure *dioxime* at 156—159°. *Isobutyryldinitroethane*, $CH_3\cdot C(N_2O_4)\cdot COPr^{\beta}$, from ethyl isopropyl ketone, melts at 58°; *isovaleryldinitroethane*, $CH_3\cdot C(N_2O_4)\cdot CO\cdot CH_2Pr^{\beta}$, from ethyl isobutyl ketone, is also crystalline; both have an odour resembling that of camphor. C. F. B.

Electrolysis of Salts of Organic Acids. By J. F. CARL SCHALL (*Zeit. Elektrochem.*, 1896, **3**, 83).—Dithiocarboxylic acids, or their salts with the alkali metals, are decomposed by electrolysis of their aqueous solutions according to the equation $2R\cdot CSSM = 2R\cdot CSS + 2M$; and $2RCSS = (RCS)S - S(SCR)$. The author thinks it probable that the carboxylic acids decompose primarily in the same way, the peroxide thus formed subsequently decomposing into the corresponding anhydride and oxygen or into carbonic anhydride and the corresponding hydrocarbon. T. E.

Action of Bromine and Hydrogen Bromide on Ethylic Acetate. By BOLESLAS EPSTEIN (*Compt. rend.*, 1897, **124**, 688—689).—When ethylic acetate and bromine, in molecular proportion, are heated together in sealed tubes, there is, contrary to the statement of Crafts (*Compt. rend.*, 1863, **56**, 707) a considerable formation of hydrogen bromide, the other products being ethylic bromide and monobromacetic acid without any appreciable quantity of ethylic monobromacetate. Ethylic α-monobromopropionate under the same conditions at 180—200°, yields a considerable quantity of hydrogen bromide, together with ethylic bromide, ethylic dibromopropionate, and dibromopropionic acid, the proportion of the dibromopropionate increasing considerably with the time of heating.

It would seem that the products result from two successive reactions, $CMeHBr{\cdot}COOEt + Br_2 = CMeBr_2{\cdot}COOEt + HBr$ and $CMeBr_2{\cdot}COOEt + HBr = EtBr + CMeBr_2{\cdot}COOH$, the latter being reversible and the rate of change being different in the two directions. C. H. B.

Fatty Substances found in Egyptian Tombs at Abydos. By Charles Friedel (*Compt. rend.*, 1897, **124**, 648—653).—The substances described in this paper were found in earthen vases in the interior of Egyptian tombs which are believed to be earlier than the first dynasty. They were no doubt intended as provision for the dead; the specimens examined included.

(1) Several kilos. of a pale brown, porous, granular substance, covered with a black outer layer. It consists of palmitic acid mixed with less than 51 per cent. of palmitin, and there can be little doubt that the original substance was palm oil, which, in course of time, has been gradually oxidised, and partially saponified owing to the readier oxidation of the glycerol. Some acids of the succinic series (? azelaic and pimelic) are also present. The outer black layer seems to be the oxidation product of some resinous substance, used probably to protect the palm oil.

(2) A firmer, more granular, paler mass, consisting of stearic acid, with about 30 per cent. of stearin, the original substance being in all probability beef or mutton fat.

(3) A dark brown, granular cake, consisting of palmitic acid, with 41 per cent. of palmitin.

(4) A pale yellow-brown, light, porous mass, which gives off but little odour when it burns, and leaves a considerable quantity (about 46 per cent.) of ash of the composition SO_2, 13·67; CaO, 31·42; Al_2O_3 and Fe_2O_3, 9·34; K_2O, 15·04; Na_2O, 1·33. It contains grape seeds and also some seeds which seemed to be a cereal, and there is little doubt that the original substance was a cake made of raisins and some cereal.

Some small vases were found to contain powdered galena mixed with some fatty matter, doubtless for use as a cosmetic. C. H. B.

Formulæ of Cerotic and Melissic Acids. By Theod. Marie (*Bull. Soc. Chim.*, 1896, [iii], **15**, 565—569).—The author has endeavoured to fix more definitely the formulæ of cerotic and melissic acids obtained from bees-wax. The analysis of the free acids, of their ethereal salts, and of numerous derivatives point to the identity of melissic acid obtained from carnauba wax with that obtained from bees-wax. The formula $C_{30}H_{60}O_2$, generally accepted for the former acid, must therefore be assigned to the latter. The free melissic acid extracted from bees-wax is also identical with that obtained by the action of soda-lime on myricylic alcohol. In the case of cerotic acid, the numbers obtained in the analysis of the acid itself, its ethereal salts, the salts of barium and silver, and eight of its derivatives indicate that this acid must be represented either by the formula $C_{25}H_{50}O_2$ or $C_{26}H_{52}O_2$, the former being the more probable. In any case, Brodie's formula, $C_{27}H_{54}O_2$, must be rejected. By the action of concentrated hydriodic acid and red phosphorus on the acid at 210—240°, a hydrocarbon was obtained readily soluble in ether and benzene, insoluble in alcohol, and melting at 54°. Its formula is either $C_{25}H_{52}$ or $C_{26}H_{54}$. In the former case, it would be placed between the hydrocarbons tetracosane (m. p. 51·1°) and heptacosane (m. p. 59·5°) prepared by Krafft. In addition to this hydrocarbon, an acid is also formed in the above reaction melting at 95°, and therefore considerably above cerotic acid itself (77·5°). This is in accordance with Krafft's observations on the action of hydriodic acid on the lower fatty acids. It appears almost certain that $C_{25}H_{50}O_2$ represents the composition of cerotic acid and that it therefore follows lignoceric acid in the series. A. C. C.

Bromo-derivatives of Cerotic and Melissic Acids. By THEOD. MARIE (*Bull. Soc. Chim.*, 1896, [iii], 15, 569—575).—*Bromocerotic acid*, $C_{24}H_{48}Br\cdot COOH$, is obtained by acting on cerotic acid with the theoretical quantity of bromine in the presence of red phosphorus, the mixture being at first kept cool and finally heated at 100° until the evolution of hydrogen bromide ceases. It is very soluble in benzene, from which it crystallises on evaporation in mammilated masses consisting of fine needles melting at 66·5°. It is very stable, but when heated to 220—250° undergoes decomposition with disengagement of gas. *Ethylic bromocerotate*, $C_{24}H_{48}Br\cdot COOEt$, is obtained when a solution of the above acid in 95 per cent. ethylic alcohol is boiled for 3 hours with the addition of sulphuric acid. It is more soluble in alcohol than either cerotic acid or its bromo-derivative, and crystallises from this solvent in felted masses of fine needles melting at 46·5°.

Dibromocerotic acid, $C_{24}H_{47}Br_2\cdot COOH$, is prepared by the action of excess of bromine on the monobromo-derivative in presence of red phosphorus. The product of the reaction is dissolved in hot benzene, from which, on cooling, crystals of the monobromo-derivative are first obtained; the mother liquors, on concentration, yield a crystalline mass of the dibromo-derivative melting at about 30°.

Bromomelissic acid, $C_{29}H_{58}Br\cdot COOH$, is obtained in a similar manner to the corresponding cerotic acid derivativte; it crystallises from hot benzene in small masses consisting of radiating needles melting at 79·5°. The *ethylic* salt of this acid, prepared similarly to the corresponding cerotate, crystallises from boiling alcohol in fine, long needles melting at 65°. *Dibromomelissic acid*, $C_{29}H_{57}Br_2\cdot COOH$, is obtained in a similar manner to dibromocerotic acid. The benzene solution of the products of the action yields first the monobromo-derivative and then, on complete evaporation of the solvent, a yellowish residue melting at 47°, and consisting almost entirely of the dibromo-acid. In this experiment, the displacement of the second hydrogen atom takes place with much greater difficulty than the first. Hitherto, the dibromo-derivatives of the higher fatty acids have only been obtained by the addition of bromine to the corresponding unsaturated acids. A. C. C.

Comparison of the Derivatives of Cerotic and Melissic Acids with those of the Fatty Acids. By THEOD. MARIE (*Bull. Soc. Chim.*, 1896, [iii], 15, 590—591).—A study of the chemical and physical properties of the derivatives of cerotic and melissic acids shows that these acids have a precisely similar constitution to palmitic and stearic acids, and that they are, in fact, true fatty acids. It is pointed out that the same methods of preparation are applicable in both cases, and that the melting points and solubilities are in direct relation with their increased molecular weights. A table is given in which the melting points of 15 derivatives of cerotic and melissic acids are compared with those of the corresponding derivatives of myristic, palmitic, and stearic acids. A. C. C.

Decomposition of Ethoxalic Chloride [Ethylic Chloroglyoxylate] with Elimination of Carbonic Oxide. By GIUSEPPE GRASSI-CRISTÁLDI (*Gazzetta*, 1897, 27, i, 27—34).—W. Wislicenus has shown (Abstr., 1894, i, 323) that derivatives of ethylic oxalacetate decompose when heated, liberating carbonic oxide, and the author finds that, on passing the vapour of ethylic chloroglyoxylate (Anschütz, Abstr., 1886, 1011) through a glass tube heated at 200°, and cooling the product in a freezing mixture, ethylic chlorocarbonate is produced, in accordance with the equation $COCl\cdot COOEt = CO + Cl\cdot COOEt$.

When the vapour of ethylic oxalate is passed through a glass tube at a low red heat, it decomposes in accordance with the equation: $COOEt\cdot COOEt = CO_2 + C_2H_4 + H\cdot COOEt$; no carbonic oxide is produced, but a little formic acid is obtained owing to secondary action.

W. J. P.

Hydroxy- and Amido-derivatives of Cerotic and Melissic Acids. By THEOD. MARIE (*Bull. Soc. Chim.*, 1896, [iii], 15, 576—583). —*Hydroxycerotic acid*, $OH\cdot C_{24}H_{48}\cdot COOH$, is obtained by the action of caustic soda on the monobromo-derivative in alcoholic solution. When crystallised, first from light petroleum and then from alcohol, in which it is very soluble, it forms tufts of fine radiating needles melting at 86·5°. From benzene, it crystallises in microscopic needles. It may also be prepared by the action of lead acetate on ethylic bromocerotate. *Ethylic acetoxycerotate*, which is first formed, crystallises from ether in colourless needles melting at 57—58°. This compound on saponification with caustic potash in alcoholic solution yields the hydroxy-acid. The salts of barium and magnesium are obtained as white, flocculent precipitates on mixing alcoholic solutions of the acid and of the metallic acetates. When heated at 170—200°, 2 molecules of hydroxycerotic acid lose 1 molecule of water, yielding a colourless substance, which does not unite with bromine, is soluble in ether and benzene, and melts at 76—77°. This anhydride, when heated with a dilute aqueous solution of caustic potash, undergoes conversion into the original acid.

Amidocerotic acid, $NH_2\cdot C_{24}H_{48}\cdot COOH$, is prepared by the action of ammonia on bromocerotic acid in alcoholic solution, and forms small, rounded masses of radiating needles. After heating on the water bath, and washing consecutively with water, alcohol, and boiling ether, a white, powdery crystalline residue remains, melting at 215°. It is practically insoluble in alcohol, ether, benzene, ethylic acetate, amylic alcohol, and chloroform, but dissolves in an alcoholic solution of potash and in boiling glacial acetic acid.

Hydroxymelissic acid, $OH\cdot C_{29}H_{58}\cdot COOH$, is prepared by acting on the bromo-acid with alcoholic potash. It crystallises in masses of microscopic needles, which, after three crystallisations from hot benzene, followed by two crystallisations from ether, melt at 96·5°. When heated at 190—200°, this acid undergoes an analogous decomposition to hydroxycerotic acid.

Amidomelissic acid, $NH_2\cdot C_{29}H_{58}\cdot COOH$, is prepared in a similar manner to the cerotic acid derivative. When thoroughly washed with boiling water, boiling alcohol, and ether, it forms a white powder, melting with decomposition at 205°; it dissolves in aqueous and alcoholic solutions of caustic potash and in boiling glacial acetic acid, but is insoluble in almost all the ordinary organic solvents. In the preparation of these amido-derivatives, small quantities of the hydroxy-acids are also formed.

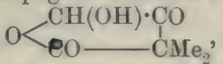
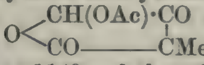
A. C. C.

Derivatives of Methylic Monobromodimethylacetoacetate.

By **Max Conrad** (*Ber.*, 1897, 30, 856—863. Compare Abstr., 1896, i, 409).—[With **Anton Kreichgauer.**]—*Methylic γ-bromodimethylacetoacetate* is readily obtained as a yellowish oil when the requisite quantity of bromine is added in the cold to methylic dimethylacetoacetate; as this oil decomposes on distillation, it is necessary to use it in the crude form.

Methylic methoxydimethylacetoacetate, $OMe\cdot CH_2\cdot CO\cdot CMe_2\cdot COOMe$, can be prepared by treating the monobromomethylic salt with sodium methoxide; after being washed with light petroleum and recrystallised from ether, it is obtained in hard, glistening crystals melting at 70° and distilling at 240—242°.

Methylic acetoxydimethylacetoacetate, $OAc\cdot CH_2\cdot CO\cdot CMe_2\cdot COOMe$, is a colourless oil which distils at 244—246°; its sp. gr. is 1·135 at 16°/15°.

Dihydroxydimethylacetoacetic acid lactone,  $\mathrm{O}<\begin{array}{l}\mathrm{CH(OH)\cdot CO}\\ \mathrm{CO}\text{———}\mathrm{CMe_2}\end{array}$, is obtained when either the methylic salt or the acetate described above is brominated in carbon bisulphide solution and then left in contact with water for several weeks. It is best purified by washing with ether; it crystallises in prisms which melt at 168—169°, at the same time evolving carbonic anhydride and yielding a white sublimate. The *acetate* of the lactone,  $\mathrm{O}<\begin{array}{l}\mathrm{CH(OAc)\cdot CO}\\ \mathrm{CO}\text{———}\mathrm{CMe_2}\end{array}$, exists in two isomeric forms, one of which melts at 114° and the other at 154°. These two compounds are being further investigated.

When this lactone is shaken with soda solution at the ordinary temperature, it is gradually dissolved, and the addition of hydrochloric acid to this solution yields, in the course of a day or two, the isomeric 2-*dimethyl*-3:4-*butanonaloic acid*, $COH\cdot CO\cdot CMe_2\cdot COOH$, melting at 138°.

The same acid can be obtained by dissolving the lactone in boiling ethylic alcohol and then precipitating with water.

[With RUPPERT.]—*β-Dimethylmalic acid*,

$$COOH\cdot CH(OH)\cdot CMe_2\cdot COOH,$$

is formed when an alcoholic solution of the lactone or of the isomeric acid is added to sodium hydroxide solution at 0°; the mixture is kept for 12 hours, and then evaporated on the water bath. The acid crystallises from boiling ethylic acetate in prisms, and melts at 129°. Its solution yields precipitates with ferric chloride and silver nitrate, but not with lead acetate, zinc sulphate, or copper sulphate.

Isobutyrylformaldehyde, 3-methyl-2-butanonal, $CHMe_2\cdot CO\cdot COH$, is the product formed when the lactone or its isomeride is boiled with water. It crystallises in prisms, melts at 95°, has a sweet taste, and is readily soluble in ether and alcohol. Its *osazone*,

$$CHMe_2\cdot C(:N_2HPh)\cdot CH:N_2HPh,$$

melts at 115°, and its *dioxime* at 110°.

When isobutyrylformaldehyde is treated with a dilute alcoholic solution of soda, it yields α-hydroxyisovaleric acid, melting at 83°.

Methylic acetoxymethoxydimethylacetoacetate,

$$OAc\cdot CH(OMe)\cdot CO\cdot CMe_2\cdot COOMe,$$

melts at 54° and distils at 220—240°, undergoing partial decomposition.

J. J. S.

Transformations of Sugars: Levulinic Acid. By MARCELLIN P. E. BERTHELOT and GUSTAVE ANDRÉ (*Compt. rend.*, 1897, **124**, 645—648). —*Levulinic Acid.*—Heat of combustion (1 gram) at constant volume 4975·2 cal., molecular heat of combustion + 577·1 Cal. at constant volume and + 577·4 Cal. at constant pressure; heat of formation from its elements, solid acid, + 170·1 Cal., liquid acid + 167·9 Cal., dissolved acid + 166·5 Cal.

Levulinic lactone or olide (liquid).—Heat of combustion (1 gram) 6112·0 cal., molecular heat of combustion + 599·2 Cal. at constant volume and + 599·5 Cal. at constant pressure; heat of formation from its elements + 79·0 Cal.; heat of hydration (liquid anhydride, liquid water, and liquid acid) + 19·9 Cal., which is higher than the corresponding value for most organic anhydrides.

The formation of levulinic acid from glucose, $C_6H_{12}O_6$ diss. + $C_5H_8O_3$ diss. + $H\cdot COOH$ diss. + H_2O, should therefore develop + 36·7 Cal. The conversion of dissolved glucose into dissolved alcohol and gaseous carbonic anhydride develops + 33·0 Cal., and its conversion into dissolved lactic acid develops + 34 Cal. It is evident, therefore, that all three transformations of glucose are exothermic, and they develop practically the same quantities of heat. The conversion of glucose into acetic acid, if possible, would develop + 51·8 Cal., and the synthesis of glucose from formaldehyde would develop + 57·6 Cal., if + 40·4 Cal. be accepted as the heat of formation of dissolved formaldehyde. The conversion of glucose into formaldehyde would, on the other hand, absorb − 57·6 Cal.

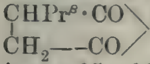
Glucose behaves as a particularly mobile molecule, and this is doubtless due to its formation from aldehydic groups, the hydrogen and oxygen atoms oscillating between several carbon centres. The authors suggest that in the production of alcohol it is not the living cell itself but some compound secreted by it that brings about the transformation of the glucose. C. H. B.

Synthesis of δ-Dimethyl-levulinic Acid. By MAX CONRAD (*Ber.*, 1897, **30**, 864—865).—Few attempts seem to have been made to condense the γ-bromo-derivatives of ethylic dialkylacetoacetates with the sodium compound of ethylic malonate, although by this means many compounds could be synthetically prepared the formation of which by other methods would be long and tedious.

Ethylic bromodimethylacetoacetate reacts readily with methylic sodiomalonate, and although the yield is somewhat decreased by the formation of methylic ethanetetracarboxylate, yet a moderately large quantity of the condensation product, *methylic 1-dimethyl-2-keto-4-carboxyadipate*, $(COOMe)_2\cdot CH\cdot CH_2\cdot CO\cdot CMe_2\cdot COOMe$ [*ketoisohexane-ααδ-tricarboxylate*], is obtained as a thick oil boiling at 300—320° with partial decomposition.

On hydrolysing the methylic salt with dilute sulphuric acid, 2 molecules of carbonic anhydride are eliminated, and *δ-dimethyl-levulinic acid*, $COOH\cdot CH_2\cdot CH_2\cdot CO\cdot CHMe_2$, is formed. This acid crystallises from warm, light petroleum in long, colourless needles melting at 40—41°, and is identical with the acid obtained by Fittig from isoheptenic acid.

J. F. T.

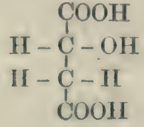
Action of Potassium Cyanide on 1 : 4-Olides [Lactones]. By EDMOND BLAISE (*Compt. rend.*, 1897, **124**, 89—91).—When isocaprolactone is heated in a sealed tube for 5 hours at 270—280° with potassium cyanide and the product treated with acetic chloride, an acid anhydride melting at 240—250° is obtained. This reacts with aniline, forming the compound $COOH\cdot CHPr^{\beta}\cdot CO\cdot NHPh$, which crystallises from benzene in nacreous plates melting at 142—144°, and on boiling with dilute hydrochloric acid yields isopropylsuccinic acid melting at 118°. When the above aniline derivative is kept for some minutes at its boiling point, it undergoes conversion into the compound  $\left.\begin{array}{l}CHPr^{\beta}\cdot CO\\ |\\ CH_2{-}{-}CO\end{array}\right>NPh$, which crystallises from dilute alcohol in needles melting at 95—96°. Had the action of potassium cyanide on the above lactone been analogous to the reactions occurring in the cases studied by Wislicenus (Abstr., 1886, 879), the acid $COOH\cdot CMe_2\cdot CH_2\cdot CH_2\cdot COOH$ would have been formed instead of isopropylsuccinic acid.

A. C. C.

Cyanide and a Dibasic Acid and its Amide derived from Cerotic Acid. By THEOD. MARIE (*Bull. Soc. Chim.*, 1896 [iii], **15**, 583—590).—*Cyanocerotic acid*, $CN\cdot C_{24}H_{48}\cdot COOH$, is prepared by the action of potassium cyanide on ethylic bromocerotate in alcoholic solution. On treating the aqueous solution of the potassium salt of this acid with dilute sulphuric acid, the acid separates as a transparent precipitate which becomes opaque on boiling. From benzene, it is obtained in rounded masses, consisting of fine needles melting constantly at 86°, whilst from ether it melts at 88°. When heated at 180—190°, it undergoes partial decomposition into carbonic anhydrile and cerotonitrile, $C_{24}H_{49}\cdot CN$, melting at 58—59°, and identical with the product of the dehydration of cerotamide (this vol., i, 266).

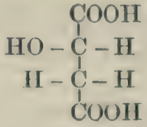
The *amic acid*, $NH_2 \cdot CO \cdot C_{24}H_{48} \cdot COOH$, is obtained when the preceding acid is boiled for 12 hours with caustic potash in alcoholic solution. When separated from its potassium salt by the addition of a dilute mineral acid, it is obtained as a granular precipitate by pouring its alcoholic solution into ether. From hot benzene, it crystallises in bundles of fine needles, radiating from a point. When heated to 160°, it undergoes decomposition, carbonic anhydride being evolved and cerotamide, melting at 109—110°, formed. The decomposition is, however, not complete, the residue always containing some of the unaltered acid. By the prolonged action of an alcoholic solution of caustic potash on the preceding acid, or on cyanocerotic acid itself, the *dibasic acid*, $C_{24}H_{48}(COOH)_2$, is obtained, together with hydroxycerotic and cerotic acids, from which it can only be separated with very great difficulty. By fractional precipitation with barium acetate, a barium salt was prepared containing very nearly the percentage of barium required for the salt of the dibasic acid; from this an acid was obtained melting at 112—114°. When heated to 150°, it readily decomposes into carbonic anhydride and cerotic acid. The author is of opinion that the bromine atom in monobromocerotic acid is in the α-position relative to the carboxyl group. A. C. C.

Optical Behaviour of Malic Acid. By CHR. WINTHER (*Chem. Centr.*, 1896, ii, 22—23; from *Nyt Tidsskrift Fysik Kemi*, 1896, 122—131).—After giving an account of the relation of malic acid and the malates to Oudemans' law, the author shows how Nasini's and Gennari's assumption of two active components may be explained on the asymmetrical constitution of malic acid by supposing two active ions to be formed in solution. Like all dicarboxylic acids, malic acid is first dissociated into a monocarboxylic acid. Walden's conversion of the one active variety into the other by means of phosphorus pentabromide is explained, the formulæ I and II being attributed to these compounds. On rotating II, the formula III is obtained, and the transformation is seen to consist merely in a change of position of the hydroxyl group.



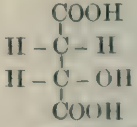
$$\begin{array}{c} COOH \\ | \\ H-C-OH \\ | \\ H-C-H \\ | \\ COOH \end{array}$$

I.



$$\begin{array}{c} COOH \\ | \\ HO-C-H \\ | \\ H-C-H \\ | \\ COOH \end{array}$$

II.



$$\begin{array}{c} COOH \\ | \\ H-C-H \\ | \\ H-C-OH \\ | \\ COOH \end{array}$$

III.

Water is first split off and then hydrogen bromide added. Now the two carboxyl groups are not of equal value, the one being influenced by the proximity of the hydroxyl group, and by assuming these groups to possess a strong intramolecular attraction, whilst in bromosuccinic acid the bromine has a repulsive action on the carboxyl group, then it follows that the bromine will not take the place of the hydroxyl group, and so the change is effected. On this hypothesis, all compounds of constitution analogous to malic acid should be capable of similar transformations; for instance, aspartic acid (by

removal of ammonia), ethoxysuccinic acid (by removal of alcohol), propylenediamine, &c.
E. W. W.

Ketocarboxylic Acids: β-Acetylglutaric Acid. By William O. Emery (*Annalen*, 1897, **295**, 94—126).—*β-Acetylglutaric acid*,

$$COMe\cdot CH(CH_2\cdot COOH)_2,$$

is obtained by heating ethylic β-acetyltricarballylate with concentrated hydrochloric acid, and submitting the anhydride produced in this way to the action of water in sealed tubes; it crystallises in aggregates of deliquescent needles, and melts indefinitely at 47—50°. The ketodilactone, $C_7H_8O_4$, the initial product of the change (Abstr., 1891, 422), crystallises in long, lustrous needles, melts at 101—102°, and boils at 205° under a pressure of 12 mm.; it resists the action of sodium carbonate, and is only in part converted into β-acetylglutaric acid when crystallised from concentrated hydrochloric acid. The *dimethylic* salt of β-acetylglutaric acid boils at 144° under a pressure of 12 mm., and has a sp. gr. = 1·1441 at 20°/4°; the *diethylic* salt boils at 154° under a pressure of 11—12 mm., and has a sp. gr. = 1·0798 at 20°/4°. The *hydrogen methyl* salt crystallises in needles, and melts at 99°; distillation resolves the substance into methylic alcohol and the ketodilactone. When the dimethylic salt is mixed with phenylhydrazine, water is eliminated, and the compound $C_{15}H_{20}N_2O_4$ produced; it crystallises from dilute acetic acid in slender needles, and melts at 83°. The *sodium* and *hydrogen sodium* salts are crystalline, and the *hydrogen potassium* salt separates from the aqueous solution in slender needles, but the *potassium* salt is deliquescent and syrupy; the *barium* salt crystallises from water with $1H_2O$, and from alcohol with $3H_2O$. The *strontium* salt contains $2H_2O$, and the calcium salt is a syrup; the *magnesium* and *silver* salts are anhydrous, and the *copper* salt contains $1H_2O$.

Ammonium β-acetylglutaramate, $C_7H_{14}N_2O_4$, produced when the ketodilactone is treated with ammonia, crystallises from a mixture of ether and alcohol in white needles melting at 141—142°. The *ketolactoneimide* of β-acetylglutaric acid, $C_7H_9NO_3$, is obtained by adding sufficient 50 per cent. acetic acid to liberate ammonia from the ammonium salt of β-acetylglutaramate; it crystallises from methylic alcohol in highly refractive prisms, and melts at 144—145°. The monimide combines with phenylhydrazine at 130°, forming the *compound*

$$C_{13}H_{15}N_3O_2,$$

which crystallises from methylic alcohol in microscopic octahedra and melts at 228—229°.

The *ketodiimide* of β-acetylglutaric acid, $C_7H_{10}N_2O_2$, is obtained by heating ethylic β-acetylglutarate with alcoholic ammonia, and is also produced when ammonium β-acetylglutaramate is heated at 150—160° until water vapour ceases to be liberated, or when the monimide is heated at 150° in an atmosphere of ammonia; it crystallises from methylic alcohol, and melts above 275°, at which temperature it darkens. Acetic anhydride has no action on the ketodiimide at 100°, but in sealed tubes at 150—160° it is converted into an *acetyl* derivative, $C_9H_{12}N_2O_3$, which crystallises from benzene in snow-white plates and melts at 142—144°.

The *ketolactonanil*, $C_{13}H_{13}NO_3$, is obtained by the action of aniline on the ketodilactone dissolved in absolute alcohol or chloroform; it crystallises from a mixture of ether and ethylic acetate in colourless leaflets, and melts at 154°. It dissolves in concentrated sulphuric acid without undergoing change, and is also soluble in ammonia, being deposited again on evaporation. The *ketoanilimide*, $C_{13}H_{14}N_2O_2$, produced when the foregoing substance is heated with alcoholic ammonia in sealed tubes at 100°, separates from alcohol in small, compact crystals, and melts at 207·5°. The *ketolactonorthotolil*, $C_{14}H_{15}NO_3$, crystallises from hot water in aggregates of small needles and melts at 138°; the *paratolil* crystallises from methylic alcohol in colourless leaflets and melts at 135°. The *ketoparatolilimide*, $C_{14}H_{16}N_2O_2$, is obtained from the paratolil and alcoholic ammonia, and crystallises from methylic alcohol in microscopic prisms melting at 189°. The *ketolacton-α-naphthil* and the *ketolacton-β-naphthil*, $C_{17}H_{15}NO_3$, melt at 153° and 186° respectively.

The *ketobisphenylhydrazide anhydride*, $C_{19}H_{20}N_4O_2$, obtained by heating the ketodilactone with phenylhydrazine (2 mols.), crystallises from dilute acetic acid in small needles melting at 222—223°; the *acetyl* derivative melts at 243°. The *ketolactonephenyl-α-ethylhydrazide anhydride*, $C_{15}H_{18}N_2O_3$, is produced on heating the ketodilactone with α ethylphenylhydrazine (1 mol.) at 160°, and melts at 195°; both hydrazine compounds give a rose-coloured solution in concentrated sulphuric acid, which becomes dark red on the addition of ferric chloride.

Reduction of the ketodilactone with sodium amalgam gives rise to the lactonic *acid*, $C_7H_{10}O_4$, which crystallises in small needles, melts at 78—79°, and boils at 225° under a pressure of 20 mm.; the *silver* salt forms colourless, microscopic crystals.

Hydriodic acid converts the ketodilactone into β-ethylglutaric acid, which melts at 73° (compare Komnenos, *Annalen*, **218**, 167).

M. O. F.

Lyxonic Acid and Lyxitol.—By GABRIEL BERTRAND (*Bull. Soc. Chim.*, 1896, [iii], **15**, 592—594).—The author gives an account of the results he had obtained in the study of lyxonic acid and some of its derivatives at the time of the publication of a paper on the same subject by Fischer and Bromberg (Abstr., 1896, i, 348). For the separation of lyxonic acid from its stereoisomeride, xylonic acid, advantage is taken of the slight solubility of a compound of cadmium xylonate with cadmium bromide, the lyxonic acid being separated from the mother liquors.

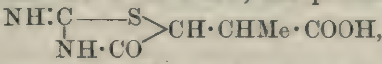
The phenylhydrazide of lyxonic acid crystallises with $2H_2O$ (compare Abstr., 1896, i, 667) and melts at 142°, but when anhydrous at 148—149°. No crystalline phenylhydrazide of xylonic acid could be prepared. By the reduction of the lactone of lyxonic acid, lyxose was obtained, and this, on further reduction with sodium amalgam, yielded lyxitol as a nearly colourless syrup. No compound of lyxitol with benzaldehyde could be obtained.

Directions are given for the preparation of xylonic acid in quantity from molasses.

A. C. C.

Cryoscopic Determination of the Constitution of Amides. By ARTHUR LACHMANN (*Zeit. physikal. Chem.*, 1897, **22**, 170—172).—

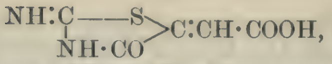
Auwers has shown that hydroxy-compounds are, in general, cryoscopically abnormal, as also are very many acid amides (Abstr., 1894, ii, 133; 1895, ii, 41). As the amides are probably divisible into two classes, the true amides and the imido-compounds $R\cdot C(OH)\cdot NH$, it is possible that the abnormal behaviour is characteristic of the latter. Oxamethane has been shown by Wallach to contain no hydroxyl group, and the author therefore studied its cryoscopic behaviour, employing methylic oxalate as a solvent. The molecular weight obtained varied from 114 to 226, so that this compound also behaves abnormally, and the abnormality is not an indication of the hydroxylic nature of the amide. L. M. J.

Thiohydantoins. IV. By Rudolf Andreasch (*Monatsh.*, 1897, 18, 56—94. Compare Abstr., 1896, i, 89, &c.).—Citraconic acid, or its anhydride, condenses with thiocarbamide when the two substances are heated together at 110—125° for 1—2 hours; the product is *thiohydantoin-α-propionic acid*,  $\left.\begin{array}{l}NH{:}C{-}{-}S\\ NH\cdot CO\end{array}\right>CH\cdot CHMe\cdot COOH$, and the yield 80 per cent. of the theoretical. This acid melts at 224—225°; the *barium*, $(C_6H_7N_2SO_3)_2Ba$, and basic *copper*, $C_6H_7N_2SO_3\cdot Cu\cdot OH$, salts were prepared, and also the *hydrochloride*, $C_6H_8N_2O_3,HCl$. Boiling with aqueous barium hydroxide hydrolyses the acid to *thiohydroxypyrotartaric acid*, $COOH\cdot CH(SH)\cdot CHMe\cdot COOH$; this was not obtained in well-defined crystals; when treated with benzylic chloride in alkaline solution, it yields a *benzyl* derivative which melts at 145° (uncorr.); its *barium* salt, $C_5H_6SO_4Ba + H_2O$, was also prepared. Cyanamide should also have been a product of the hydrolysis, but it could not be found; it is, however, possible to synthesise thiohydantoinpropionic acid from cyanamide and thiohydroxypyrotartaric acid. Thiohydantoin-α-propionic acid is oxidised by barium chlorate and hydrochloric acid to carbamide and a *sulphonic acid*, $COOH\cdot CH(SO_3H)\cdot CHMe\cdot COOH$, identical with that obtainable from citraconic acid and ammonium hydrogen sulphite; the *barium* salt of this acid, $(C_5H_5SO_7)_2Ba_3 + 6H_2O$, was prepared. With ferric chloride, it gives a transient violet coloration, as do all thiohydroxy-acids; the ferric chloride acts as a carrier of oxygen, and the solution, when it has lost its violet colour, is found to contain *bisthiopyrotartaric acid*, $S_2[CH(COOH)\cdot CHMe\cdot COOH]_2$, a syrup, the *barium* salt of which, $C_{10}H_{10}S_2O_8Ba_2 + H_2O$, was prepared.

Citraconic acid will also condense with substituted thiocarbamides. With symmetrical dimethylthiocarbamide, it yields *dimethylthiohydantoin-α-propionic acid*, which was obtained as an amorphous solid; the *barium* salt, $(C_8H_{11}N_2SO_3)_2Ba$, was prepared. With allylthiocarbamide, *allylthiohydantoin-α-propionic acid* is obtained as a syrup; the *barium* salt, $(C_9H_{11}N_2SO_3)_2Ba$, was prepared. With phenylthiocarbamide, it yields *phenylthiohydantoin-α-propionic acid*, which is crystalline, and melts at 214°. With diphenylthiocarbamide, it yields *diphenylthiohydantoin-α-propionic acid*, melting at 124°.

Attempts to make thiocarbamide condense with crotonic, cinnamic, and oleic acids, and with allylic alcohol, were unsuccessful. It is, thus, only with unsaturated dibasic acids that it will condense.

With bromomaleic acid, thiocarbamide yields *dehydrothiohydantoin-*

acetic acid, 
$\begin{array}{l}\mathrm{NH{:}C{-}{-}{-}S} \\ \;\;| \\ \mathrm{NH\cdot CO}\end{array}\!\!>\mathrm{C{:}CH\cdot COOH}$, which turns brown at 200°, and quite dark at 230—240°, without actually melting; sodium amalgam reduces it to thiohydantoinacetic acid, but this is for the most part hydrolysed by the alkali present to thiomalic acid (the benzyl derivative of which, $C_{11}H_{12}SO_4$, melts at 180—181°). It was hoped that the action of ammonia on it might lead to the formation of an amidothioacid, which would have been of physiological interest; this is not the case, however. When bromomaleic acid is boiled with excess of aqueous potassium hydrosulphide, *hydrothiomaleic*, $\mathrm{COOH\cdot C(SH){:}CH\cdot COOH}$, and some *thiodimaleic acid*, $\mathrm{S[C(COOH){:}CH\cdot COOH]_2}$, are formed; the former is a syrup, and yields a *benzoyl* derivative, $C_{11}H_{10}SO_4$, melting at 175°; the latter melts and decomposes at 205°. The *benzyl* derivative of thioglycollic acid, $C_9H_{10}SO_2$, was also prepared; it melts at 60°. Thiohydantoin and β-methylthiohydantoin (from α-bromopropionic acid and thiocarbamide) unite with bromine (2 atoms) in acetic acid solution, forming *dibromine* additive products, $C_3H_4N_2SO,Br_2$ and $C_4H_6N_2SO,Br_2$; both of these are crystalline substances, and the second one melts at 176—177°; the bromine is entirely removed from them by aqueous silver nitrate or sulphurous acid. Methylhydantoin also unites with hydrogen bromide in acetic acid solution, forming a compound, $C_4H_6N_2SO,HBr$, which is readily decomposed by alkalis.

C. F. B.

Mercurocarbamide and its Salts. By G. Ruspaggiari (*Gazzetta*, 1897, **27**, i, 1—13).—Carbamide combines with mercuric salts, forming salts of a bivalent radicle, $\mathrm{CO(NHHg)_2}$, which the author terms mercurocarbamide, and does not yield simple additive compounds; the reactions of the salts of this radicle with potassium iodide, sodium thiosulphate, and ammonium bromide are analogous to those of mercurammonium (Balestra, Abstr., 1893, ii, 278), carbamide being liberated in each case.

Mercurocarbamide hydroxide, $\mathrm{CO(NH\cdot Hg\cdot OH)_2}$, was obtained by Liebig (*Annalen*, **85**, 289) by precipitating mercuric nitrate with an alkaline solution of carbamide, and may also be prepared by boiling yellow mercuric oxide with a solution of carbamide; Dessaignes (*Annalen*, **82**, 232) obtained a double compound of the composition $\mathrm{CO(NH\cdot Hg\cdot OH)_2,CO(NH_2)_2}$ by boiling excess of concentrated carbamide solution with mercuric oxide. The *chloride*, $\mathrm{CO(NHHgCl)_2}$, is obtained by adding a solution of carbamide in sodium hydrogen carbonate solution to mercuric chloride solution; it crystallises in microscopic, white pyramids, is insoluble in water, and is not affected by light. On boiling carbamide with mercuric chloride solution, a double *salt* of the composition $\mathrm{CO(NHHgCl)_2,CO(NH_2)_2,2HCl}$ is formed and separates on cooling in long, colourless needles; it corresponds with the compound, $\mathrm{CO(NH_2)_2,HgCl_2}$, described by Werther (*J. pr. Chem.*, **35**, 5).

Mercurocarbamide nitrate, $\mathrm{CO(NH\cdot Hg\cdot NO_3)_2}$, separates as a gelatinous, white mass on mixing methylic alcoholic solutions of mercuric nitrate and carbamide; it is decomposed by water. The basic *nitrate*, $\mathrm{OH\cdot Hg\cdot NH\cdot CO\cdot NH\cdot Hg\cdot NO_3 + H_2O}$, obtained by heating a dilute aqueous solution of mercuric nitrate with carbamide, crystallises in short hexagonal prisms, has a feeble alkaline reaction, and is the compound obtained when Liebig's method of determining carbamide is properly carried out.

Mercurocarbamide sulphate, $CO\colon(NH{\cdot}Hg)_2\colon SO_4$, prepared from carbamide and mercuric sulphate, crystallises in tiny pyramids and is soluble in water. The *acetate*, $CO(NH{\cdot}Hg{\cdot}OAc)_2$, crystallises in thin, microscopic needles and is insoluble in the ordinary solvents.

W. J. P.

Triethylsulphine Metaaluminate. By UGO ALVISI (*Zeit. anorg. Chem.*, 1897, **14**, 302—308).—Triethylsulphine metaaluminate is formed by the action of a solution of triethylsulphine hydroxide on aluminium. Similarly to the solution of aluminium in sodium hydroxide, hydrogen is evolved in the action, and this reacts on the unaltered free base with formation of ethylic sulphide, ethane, and water, and also on the metaaluminate with the formation of ethylic sulphide, ethane, and aluminium hydroxide. When a concentrated solution of the aluminate is heated, it is completely decomposed into ethylic sulphide, ethylene, and aluminium hydroxide; the same decomposition also takes place when the solution is evaporated in a vacuum over calcium chloride or sulphuric acid; this decomposition is similar to that which the triethylsulphine hydroxide undergoes on heating, ethylic sulphide, ethylene, and water being formed. The above decomposition explains why triethylsulphine hydroxide is not obtained by the action of ethylic sulphide on ethylic alcohol, whereas the corresponding chloride or bromide is obtained by the action of ethylic sulphide on ethylic chloride, or bromide, or on ethylenic bromide. E. C. R.

Some new Constituents of Caucasian Naphtha. By WLADIMIR B. MARKOWNIKOFF (*Ber.*, 1897, **30**, 974—977).—A comparison of the boiling points of several fractions of Caucasian naphtha, with their specific gravities, showed certain irregularities; for instance, it was noticed that, between the fractions 58—48° and 48—46°, the sp. gr. fell from 0·712 to 0·666, and this could only be explained by supposing the presence of cyclic hydrocarbons in the mixture.

On nitrating the fractions 48—50° and 50—51°, a nitro-derivative was obtained which, on reduction, yielded an amine, which gave a characteristic benzoyl derivative, crystallising from alcohol in transparent, quadratic plates melting at 157·5—158·5°, and identical with the benzoyl derivative of amidocyclopentane prepared by Wislicenus' method. A large quantity of a crystalline acid was also produced during the process of nitration; this crystallised from water in large, quadratic plates melting at 96·5—97°, and corresponded in every respect with glutaric acid. Similarly, the fraction containing hexamethylene, on treatment with nitric acid, yielded adipic acid. It is, therefore, certain that cyclic hydrocarbons, containing no side chains, pass on oxidation with nitric acid into the corresponding dibasic acids.

Investigation of the fraction 90·5—98° showed the presence of a hydrocarbon, C_7H_{14}, containing a side chain; on nitration, this yielded a tertiary nitro-derivative of the formula $C_7H_{13}{\cdot}NO_2$, and boiling at 98—99° (40 mm.); the tertiary amine obtained on reduction boiled at

131—132°, and the tertiary alcohol was prepared from the amine by treatment with sodium nitrite at 144—145°. As a bye-product in the preparation of this alcohol, an unsaturated hydrocarbon of the formula C_7H_{12} was obtained. J. F. T.

The Benzene Nucleus. By WILHELM VAUBEL (*J. pr. Chem.*, 1897, [ii], **55**, 221—224. Compare Abstr., 1896, i, 646).—The author points out that his formula for benzene (Abstr., 1894, i, 325) admits of a certain oscillation of the groups within the molecule; this oscillation being granted, the formula no longer indicates the possibility of enantiomorphous bi-substitution derivatives. C. F. B.

Absorption of Nitrogen by Carbon Compounds under the influence of the Silent Electric Discharge. By MARCELLIN P. E. BERTHELOT (*Compt. rend.*, 1897, **124**, 528—532).—The rate at which nitrogen is absorbed by benzene under the influence of the silent electric discharge (Abstr., 1895, ii, 469, 495, 498) is higher the more frequent the vibrations of the contact breaker. A Marcel-Deprez interrupter, with or without specially high frequency, gives better results than a Foucault interrupter. The maximum quantity of nitrogen absorbed by benzene is about 12 per cent. of the weight of the latter, and in presence of excess of benzene the absorption of chemical nitrogen is complete. In the case of atmospheric nitrogen, the absorption is incomplete, but the residue is smaller than the quantity of argon present with the nitrogen, because part of the argon is absorbed. The ratio of benzene to nitrogen, when the maximum absorption has taken place, is $3C_6H_6 : N_2$.

The empirical composition of the product corresponds with that of diphenylphenylenediamine, and it shows many of the properties of diamines of this class, mixed with products of condensation. It readily oxidises when exposed to air or oxygen, without any simultaneous liberation of nitrogen, and yields salts when treated with hydrochloric acid, the bases of these salts having odours which recall those of quinoline and the hydropyridine bases. The product formed with hydrochloric acid also yields ammonium chloride when heated. When the original product is heated, it yields large quantities of ammonia, together with benzene, water (resulting from oxidation by the air), a minute trace of aniline, and a bituminous liquid containing nitrogen compounds. When heated with special precautions to avoid previous contact with air, it yields ammonia, but no free nitrogen.

With carbon bisulphide, the absorption is more rapid than with benzene, and is complete in presence of an excess of bisulphide. With excess of nitrogen, the maximum quantity absorbed is 11·7 per cent. of the weight of the bisulphide, and the ratio is the same, $3CS_2 : N_2$. The product readily oxidises in contact with oxygen, and no appreciable quantity of nitrogen is liberated. When heated without having been in contact with air or oxygen, a certain proportion of the nitrogen is liberated, but the greater part remains in combination with the products of condensation, and it follows that the latter are more stable than the products formed by argon or helium.

Thiophen under similar conditions absorbs 8·6 per cent. of its weight of nitrogen, the ratio in this case being $2C_4SH_4 : N$. The rate of absorption is lower than with carbon bisulphide. C. H. B.

Electrolytic Reduction of Aromatic Nitro-compounds. By WALTHER LÖB (*Chem. Centr.*, 1896, i, 901—902; from *Zeit. Elektrotechn. u. Elektrochem.*, 1896, 2, 529—534).—The author gives the following explanation of the fact that nitro-compounds, when reduced in alkaline solution, form mainly azo- and azoxy-compounds whilst in acid solution, hydrazo- and amido-compounds result. By the addition of water, a hydrated derivative, $RN(OH)_4$, is first formed, and this is not dissociated in solution, as neither hydrogen nor hydroxyl ions can be supposed to be formed. In the former case, the nitro-groups must be assumed to act as an acid and to form salts, whereas, in reality, the nitro-group cannot itself confer acidity, its function being limited to increasing the previous acidity of the molecule. The formation of hydroxyl ions is confined to substances of a basic character. If the alkaline solution of the hydrate $RN(OH)_4$ is kept at the negative pole by a diaphragm, the sodium ions which are liberated there react with the hydroxyl groups to form sodium hydroxide, and so may induce the following possible reactions, according to the number of hydroxyl groups which are separated from the nitrogen:—(1) The residues $R-N\equiv$, produced by separation of four hydroxl groups, unite to form an azo-compound; (2) an azoxy-compound is formed from the residues $RN(OH)\equiv$ obtained by the separation of three hydroxyl groups; (3) two hydroxyl groups are removed and the residues $RN(OH)_2=$ combine to form a nitroso-compound; (4) one hydroxyl group is separated and the residues, $RN(OH)_3-$, unite to form an unknown compound,

$$(NO)R\cdot O\cdot R(NO).$$

Experimental results with alkaline solutions show that only the first two possibilities come into consideration. The oxygen of the nitro-groups may also be supposed to be directly withdrawn by the action of sodium ions, the oxide then uniting with water to form sodium hydroxide, but on either assumption reduction is not effected by nascent hydrogen, but by the metal in virtue of its capability of forming hydroxyl ions. Hydrazo- and amido-compounds may also be produced in alkaline solution, but this occurs only after the reduction to azo-compounds is completed, when the nascent hydrogen derived from the action of sodium on water effects a further reduction. The quantities of azo- and azoxy-compounds obtained vary according to the conditions of concentration, a kind of equilibrium being established in each case when the sodium ceases to act on the azo-compound and hydrogen begins to be evolved and to produce the hydrazo-compound by reduction of the azo-compound. Reduction in acid solution is effected by means of hydrogen ions, which, after giving up their electric charges by separating hydroxyl groups from nitrogen, go again into the condition of ions, and finally bring about the conversion of azo-compounds into hydrazo- and amido-compounds.

To effect the reduction of nitrobenzoic acid in alkaline solution, a solution of equal weights of acid and sodium hydroxide in 20 parts of water is placed in the earthenware cathode vessel and this is immersed in dilute sodium hydroxide. The electrodes are of platinum, the cathode being a cylinder 10 cm. high and 3 cm. diameter. At the ordinary temperature with 1—1·3 ampère at 6—6·5 volts, 5 grams of acid are reduced in 8—10 hours, hydrogen being liberated finally. Orthonitrobenzoic acid yields mainly orthazoxybenzoic acid with some orthohydrazobenzoic acid, the latter being separated from the former by conversion into orthodiamidodiphenic acid; meta- and paranitrobenzoic acids give the corresponding azo-acids. Neglecting small losses of nitro-compounds at the positive pole, the reduction of the meta- and para-acids is quantitative. The ortho-acid yields 50 per cent. of azoxy-acid and 5—10 per cent. of diamidodiphenic acid.

Under the same conditions, orthonitrophenol gave 60 per cent. yield of orthodiamidophenol. E. W. W.

Electrolytic Oxidation of Paranitrotoluene. By KARL ELBS (*Chem. Centr.*, 1896, i, 902; from *Zeit. Elektrotechn. w. Elektrochem.*, 1896, 2, 522—523).—On electrolysis, paranitrotoluene is oxidised only to paranitrobenzylic alcohol, and not to the corresponding acid. A yellowish, crystalline substance was also obtained. From 15 grams of paranitrotoluene, a mean yield of 7 grams of nitrobenzylic alcohol was obtained.

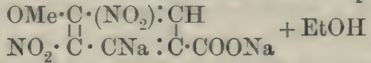
E. W. W.

Coloured Compounds obtained from Sodic Ethoxide and certain Aromatic Nitro-compounds. By C. LORING JACKSON and MARTIN H. ITTNER (*Amer. Chem. J.*, 1897, **19**, 199—216).—A number of coloured compounds obtained by the action of an alcoholic solution of sodium ethoxide on various aromatic nitro-derivatives are described. The colours are given in the following table, in which the first column gives the name and formula of the substance from which the coloured compound is prepared, the second the colour obtained, and the third the stability of the colour:

Parabromodimetanitrotoluene, $C_6H_2Br(NO_2)_2Me$	Blue.	Seconds.
Anilidodinitrotoluene, $NHPh·C_6H_2(NO_2)_2Me$	Green.	Seconds.
Amidophenyleneimidodinitrotoluene, $NH_2·C_6H_4·NH·C_6H_2(NO_2)_2Me$	Green.	Seconds.
Tribromanilidodinitrotoluene, $C_6H_2Br_3·NH·C_6H_2Me(NO_2)_2$	Purple	Minutes.
Tribromamidophenyleneimidodinitrotoluene, $NH_2·C_6HBr_3·NH·C_6H_2Me(NO_2)_2$	Bluish purple.	Minutes.
Parabromodimetanitrobenzoic acid, $C_6H_2Br(NO_2)_2·COOH$	Reddish purple.	Hours.
Ethylic parabromodimetanitrobenzoate, $C_6H_2Br(NO_2)_2·COOEt$	Rose.	Hours.
Anilidodinitrobenzoic acid, $NHPh·C_6H_2(NO_2)_2·COOH$	Pansy purple.	Hours.
Ethylic anilidodinitrobenzoate, $NHPh·C_6H_2(NO_2)_2·COOEt$	Cherry red.	Hours.
Dinitranisic (dinitromethoxybenzoic) acid, $OMe·C_6H_2(NO_2)_2·COOH$	Reddish purple.	Hours.
Dinitroethoxybenzoic acid, $OEt·C_6H_2(NO_2)_2·COOH$	Reddish purple.	Hours.
Ethylic dinitroethoxybenzoate, $OEt·C_6H_2(NO_2)_2·COOEt$	Rose.	Hours.
Chrysanisic (dinitroamidobenzoic) acid $NH_2·C_6H_2(NO_2)_2·COOH$	Black.	
Ethylic chrysanisate, $C_6H_2·NH_2·(NO_2)_2·COOEt$	Red,	

The coloured compound from dinitranisic acid was obtained as a heavy purple precipitate on adding light-petroleum to its alcoholic solution. On analysis, numbers were obtained agreeing with the formula $OMe{\cdot}C_6H_2(NO_2)_2{\cdot}COONa,NaOEt$. On heating this substance to 110°, it suffers a loss of weight corresponding nearly to 1 molecule of alcohol.

The authors suggest that, in these compounds, a hydrogen atom between a nitro-group and the methyl or carboxyl group is the one replaced by sodium, from which the formulæ of the compound from dinitranisic acid would be



$$\begin{array}{l} OMe{\cdot}C{\cdot}(NO_2){:}CH \\ NO_2{\cdot}C{\cdot}CNa{:}C{\cdot}COONa \end{array} + EtOH$$

If this hypothesis is accepted, a strongly coloured compound might be expected, which would be decomposed by water or acid giving the original substance, and the compounds containing the negative carboxyl group would be more stable than those containing methyl, both of which points hold good in the compounds described. A further point in favour of this hypothesis lies in the authors' observation that the coloured compound from dinitranisic acid gives off alcohol on heating, whilst against it is the fact that it necessitates the following assumptions :—(*a*) The existence of 1 molecule of alcohol of crystallisation in each of the substances analysed, which is improbable in compounds derived from such different sources ; (*b*) that both alcohol and water of crystallisation can be contained in the same substance ; (*c*) Lobry de Bruyn's observation that sodium does not act on trinitrobenzene even at the boiling point of xylene.

The coloured compound from bromodinitrobenzoic acid decomposes in contact with sodium ethoxide, yielding sodium bromide and dinitroethoxybenzoic acid, which combines with more sodium ethoxide forming the coloured compound of this acid. If the decomposition is allowed to go on spontaneously, sodium bromide and sodium dimetanitroparahydroxybenzoate are obtained. Similar decomposition products are produced from the compound formed by the action of sodium methoxide on bromodinitrobenzoic acid.

Dinitroethoxybenzoic acid, prepared by the action of hydrochloric acid on an alcoholic solution of ethylic chrysanisate (dinitroamidobenzoate), crystallises from alcohol in long, flat, colourless prisms, terminated by a single plane at an oblique angle. It melts at 192°, and is converted into dinitro-oxybenzoic acid on warming with dilute acids or alkalis. The *sodium* salt crystallises in easily soluble, yellow needles. A. W. C.

Action of Zinc Ethyl on Phenylic Iododichloride. By ARTHUR LACHMANN (*Ber.*, 1897, **30**, 887—888).—As the result of some experiment conducted with these substances, the author states that zinc ethyl and phenylic iododichloride combine to form an additive product which is instantly decomposed by water, forming iodobenzene. In no case does the aqueous solution give a precipitate with potassium iodide.

J. F. T.

Derivatives of Phenylic Ether. By CARL HAEUSSERMANN and EUGEN BAUER (*Ber.*, 1897, **30**, 738—741. Compare Abstr., 1896, i, 676). —*Paradihydroxyphenylic ether*, which is obtained in small amount by the action of nitrous acid on paradiamidophenylic ether, crystallises in white scales melting at 160—161°, and gives no coloration with aqueous ferric chloride. 2 : 2′-*Diamidophenylic ether* is obtained by the reduction of the corresponding nitro-compound, and crystallises in colourless needles melting at 60°; the *hydrochloride*, $O(C_6H_4{\cdot}NH_2)_2,2HCl$, crystallises in slender, white needles. When treated with sodium nitrite in acid solution, it yields a tetrazo-compound, which has not been isolated. 3-*Nitro*-4-*phenoxybenzoic acid* is prepared by heating 4-chloro-3-nitrobenzoic acid with potassium phenoxide (2 mol. prop.) at 140°; it forms indistinct, white crystals melting at 174—175°. The *barium* salt is very sparingly soluble in boiling water. The corresponding 3-*nitro*-4-*phenoxybenzenesulphonic acid* is prepared in a similar manner, and crystallises in white scales melting at 89—90°. The *potassium* salt crystallises in slender, white scales and the sparingly soluble *barium* salt in needles.

5-*Nitro*-2-*phenoxybenzoic acid* forms white, indistinct needles melting at 171—172°; the *barium* salt crystallises in white needles.

5-*Nitro*-2-*phenoxybenzenesulphonic acid* crystallises in white needles melting at 220°. A. H.

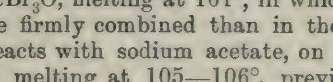
Some Derivatives of Dinitro-orthocresol. By Paul Cazeneuve (*Compt. rend.*, 1897, **124**, 154—156).—The following salts and derivatives of dinitro-orthocresol, $C_6H_2Me(NO_2)_2{\cdot}OH$ (1 : 3 : 5 : 2), are described. The *potassium* salt, $C_7H_5(NO_2)_2{\cdot}OK$, obtained by the addition of a slight excess of potash to a boiling solution of the dinitrocresol, crystallises in orange spangles; whilst the *ammonium* salt, $C_7H_5(NO_2)_2{\cdot}ONH_4 + H_2O$, prepared by saturating a solution of the dinitrocresol with ammonia, crystallises in golden yellow needles. The *barium* salt, $[C_7H_5(NO_2)_2O]_2Ba + 2H_2O$, is obtained by adding barium carbonate to a boiling solution of the dinitrocresol, and crystallises in orange needles which lose their water in a vacuum or when heated at 100°, the anhydrous salt being bright red; the *calcium* salt, $[C_7H_5(NO_2)_2O]_2Ca + H_2O$, is prepared in a similar manner; it crystallises in fine, yellow needles which lose their water at 100°, becoming bright red. All the above salts are soluble in water and alcohol.

The *acetyl* derivative, $C_7H_5(NO_2)_2{\cdot}OAc$, prepared by boiling the dinitrocresol with acetic anhydride, is colourless, insoluble in water, soluble in alcohol, ether, and benzene, and when crystallised from alcohol melts at 95°. *Nitroamino-orthocresol*, $NO_2{\cdot}C_7H_5(NH_2){\cdot}OH$ [= 3 : 5 : 2 or 5 : 3 : 2], prepared by boiling an ammoniacal, aqueous solution of the dinitrocresol with an excess of ammonium hydrosulphide, crystallises from boiling benzene in reddish-brown needles melting at 165°; it is insoluble in water, but soluble in alcohol, ether, and benzene. *Diamido-orthocresol*, $C_7H_5(NH_2)_2{\cdot}OH$ [= 3 : 5 : 2], could not be isolated, but its dihydrochloride is obtained by reducing dinitro-orthocresol by means of tin and hydrochloric acid. This salt, which crystallises in colourless needles, is soluble in alcohol and water, but insoluble in ether. A. C. C.

Halogen-derivatives of Thymol and Carvacrol. By Leo C. Urban (*Chem. Centr.*, 1896, i, 1231; from *Pharm. Rev.*, 1896, **14**, 58).—The substitution product, $(C_{10}H_{12}OI)_2$, obtained by the action of iodine on thymol, and known in commerce as aristol, can also be prepared by adding sodium hypochlorite to an alkaline solution of phenol containing an alkali iodide. The corresponding carvacrol derivative is a yellowish-brown powder melting at about 90°. The author has obtained another iodocarvacrol, a leather-coloured, amorphous powder soluble in ether, benzene, chloroform, and fatty oils, which begins to sinter at 170° and blackens at 200° without melting. The same compound is formed by adding a solution of iodine in potassium iodide to a solution of carvacrol in sodium hydroxide. The bromides of thymol and carvacrol, which, like the iodides, are derivatives of diphenol, are obtained in a similar way to the latter. Carvacrol bromide is a yellowish-grey or leather-coloured, almost odourless, powder.

E. W. W.

Constitution of Dibromo-ψ-cumenol Bromide and Similar Compounds. By KARL AUWERS (*Ber.*, 1897, **30**, 744—752. Compare Abstr., this vol., i, 34, and the two following abstracts).—Further investigation of dibromo-ψ-cumenol bromide has led the author to regard the formula proposed by Zincke, $CO\left\langle\begin{matrix}CMe{:}CBr\\CBr{:}CMe\end{matrix}\right\rangle CMeBr$, which he himself had formerly adopted, as unsatisfactory, evidence for the existence of a hydroxyl group in the compound having been obtained. When boiled with acetic anhydride, the bromide yields a *monacetate*, $C_9H_8AcBr_3O$, melting at 161°, in which the bromine atom appears to be more firmly combined than in the original compound. This monacetate reacts with sodium acetate, on continued boiling, to form the diacetate melting at 105—106°, previously described; the same compound is formed when the monacetate, $C_9H_8Br_2OAc{\cdot}OH$, which melts at 114° and is formed by the action of sodium acetate on the tribromo-compound, is boiled with acetic anhydride. When different acid radicles are introduced, however, the final di-acidyl derivatives are also different. Thus, when the monacetate melting at 161° is treated with silver isobutyrate, the compound $OAc{\cdot}C_9H_8Br_2{\cdot}O{\cdot}C_4H_7O$ is formed which melts at 79—80°. On the other hand, when the original tribromo-compound is treated with isobutyric anhydride, it yields the *isobutyrate*, $C_9H_8Br_3{\cdot}OC_4H_7O$, melting at 113°, and when this is digested with silver acetate, it is converted into the compound $OAc{\cdot}C_9H_8Br{\cdot}O{\cdot}C_4H_7O$, which is isomeric with that just described, but melts at 90—91°, and differs from it in crystalline form and other properties. The author suggests the formula



$$OH{\cdot}C\left\langle\begin{matrix}CMe{:}CBr\\ \hline CBr{:}CMe\end{matrix}\right\rangle C{\cdot}CH_2Br$$

as being in accordance with the various reactions of the substance, on the supposition that the hydroxyl group combined with the para-linked carbon atom has alcoholic and not phenolic functions. Monobromo-ψ-cumenol bromide, $C_9H_9Br(OH)Br$ (compare the following abstract), which melts at 81°, closely resembles the dibromo-compound in its behaviour towards acid radicles. The product of the action of acetic anhydride on the bromide melts at 92—93°, and when digested with silver isobutyrate yields the compound $OAc{\cdot}C_9H_9Br{\cdot}OC_4H_7O$ melting at 49—50°; the product of the action of isobutyric acid, on the other hand, melts at 91°, and on treatment with silver acetate is converted into the compound $OAc\cdot C_9H_9Br\cdot O\cdot C_4H_7O$, melting at 39—40°.

The investigation of this class of substances is being continued.

A. H.

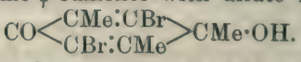
Action of Bromine on Phenol-alcohols. By Karl Auwers (*Ber.*, 1897, **30**, 753—755. Compare the foregoing abstract).—When bromine acts on a phenol-alcohol, it does not yield simple substitution products, but compounds which resemble dibromo-ψ-cumenol bromide in their behaviour. Paradimethylparahydroxybenzylic alcohol,

$$[Me_2 : CH_2\cdot OH : OH = 1 : 4 : 6 : 3],$$

is converted by 1 mol. of bromine into *monobromo-ψ-cumenol bromide*, $C_9H_{10}Br_2O$, which crystallises in long, lustrous needles, melts at 81°, and is insoluble in alkalis. On reduction, it yields monobromo-ψ-cumenol melting at 32°, which is soluble in alkalis. Excess of bromine converts it into dibromo-ψ-cumenol bromide.

Orthohydroxy-alcohols show a similar reaction; thus saligenol yields a *bromo-compound*, $C_7H_6Br_2O$, which is insoluble in alkalis and melts at 98°. The author proposes to extend the reaction to a number of different substances belonging to this class. A. H.

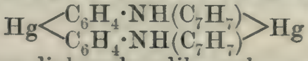
A Class of Remarkable Nitration Products of the Phenols. By Karl Auwers (*Ber.*, 1897, **30**, 755—759. Compare the two foregoing abstracts.)—Many phenols, especially such as contain several bromine atoms, resemble ψ-cumenol and its dibromo-derivative in their behaviour towards nitric acid (Abstr., 1896, i, 420) and yield characteristic nitration products which have not the properties of phenols. No such compound could be obtained from metaxylenol, but tribromometaxylenol yields a compound, $NO_2\cdot C_6Me_2Br_3O$, which, like all the substances of this class, crystallises extremely well, and melts at 97° with violent evolution of gas.

When these nitration products are heated at 100° in any solvent of sufficiently high boiling point, oxides of nitrogen are evolved and crystalline compounds free from nitrogen are formed. The substance thus obtained from the nitration product of dibromo-ψ-cumenol $C_9H_{10}Br_2O_2$, is identical with one previously prepared by Zincke (Abstr., 1896, i, 214) by boiling dibromo-ψ-cumenol with dilute nitric acid, to which he gave the formula  $CO<\begin{matrix}CMe\vdots CBr\\CBr\vdots CMe\end{matrix}>CMe\cdot OH$. This substance appears to contain a hydroxyl group, since it yields a *monacetate*, which, however, has not been obtained quite pure. The nitration product would then be represented as the nitrite of this hydroxy-derivative, $C_6Me_2Br_2O\cdot ONO$. The corresponding compound obtained from the nitration product of tribromometaxylenol melts at 173—174° and behaves in general like the foregoing. When crystallised from dilute acetic acid, it has the formula $C_8H_7Br_3O_2$, whereas when crystallised from light petroleum it has the formula $C_8H_5Br_3O$. The exact relation of these substances has not yet been determined. A. H.

Methylene Catechol [Ether]. By Charles Moureu (*Bull. Soc. Chim.*, 1897, **15**, 654—656).—Equivalent quantities of catechol and methylenic di-iodide were added to a solution of sodium ethoxide in alcohol, and the mixture was boiled for 60 hours. After distillation with steam, the product was freed from excess of methylenic di-iodide by treatment with potash. Methylene catechol ether is a colourless liquid, which boils at 172°—173°, and has sp. gr. = 1·202 at 0°.

M. W. T.

Conversion of Eugenol into Isoeugenol. By CHARLES GASSMANN (*Compt. rend.*, **124**, 38—40).—The sodium derivatives of ethylic, butylic, and amylic alcohols behave in a similar manner to the caustic alkalis in transforming eugenol into isoeugenol. With the ethoxide in alcoholic solution, it is necessary to boil for a long time, and even then the change is incomplete. The best results are obtained with sodium amyloxide in the presence of amylic alcohol, from which solvent the pure isoeugenol, boiling at 260°—262°, can readily be separated by fractional distillation. The same method may be employed for the conversion of safrole into isosafrole. A. C. C.

Organo-mercuric Compounds derived from Benzylaniline. By L. PRUSSIA (*Gazzetta*, 1897, **27**, i, 14—18).—Pesci (Abstr., 1894, i, 248) has shown that benzylamine reacts with mercuric salts, forming salts of mercurobenzylamine, and that the mercury atom, in addition to being able to combine with basic nitrogen, can also enter an aromatic nucleus, probably in the para-position (Abstr., this vol., i, 36). In continuation of Pesci's work, the author shows that a bivalent radicle of the constitution  $Hg<\begin{matrix}C_6H_4\cdot NH(C_7H_7)\\C_6H_4\cdot NH(C_7H_7)\end{matrix}>Hg$ can be formed, which he terms paramercurodiphenylenedibenzylmercurodiammonium. The *acetate* of this base, $Hg[C_6H_4\cdot NH(C_7H_7)\cdot OAc]_2Hg$, separates in thin, colourless needles on mixing alcoholic solutions of mercuric acetate and benzylaniline; after recrystallisation from benzene, it melts at 143·5—144°. It is soluble in chloroform, and on treatment with potash yields the *hydroxide*, $Hg[C_6H_4\cdot NH(C_7H_7)(OH)]_2Hg$; this crystallises with $3H_2O$ in small, colourless prisms which soften at 82·5° and melt with decomposition at 212·5°; it has an alkaline reaction and is decomposed by boiling water. The *chloride*,

$$Hg[C_6H_4\cdot NH(C_7H_7)Cl]_2Hg,$$

prepared by treating the acetate with calcium chloride, crystallises in brilliant laminæ melting at 173—174°. The *nitrate* is obtained as a crystalline, white powder on treating the hydroxide with nitric acid; it melts and decomposes at 150°.

On treating the hydroxide with sodium thiosulphate, it is converted into paramercurobenzylaniline, $Hg[C_6H_4\cdot NH(C_7H_7)]_2$, which crystallises from benzene in minute, white needles, and melts at 171·5° with partial decomposition. W. J. P.

Bromophenacetine. By WILHELM VAUBEL (*J. pr. Chem.*, 1897, [ii], **55**, 217—219).—The substance obtained by boiling bromophenacetine with potash or acids is not a liquid, but a solid melting at about 20°; it cannot, therefore, be identical with Staedel's bromoparaphenetidine. If the amido-group is replaced by hydrogen, an oil is obtained which is capable of taking up more bromine; the ethoxy-group here comes into play, and probably the formula, $NHAc{\cdot}C_6H_3Br{\cdot}OEt$ [$NHAc:Br:OEt = 1:2:4$], should be assigned to bromophenacetine.

C. F. B.

Differences between Aromatic Nitramines and Nitrosamines. By JOHANNES PINNOW (*Ber.*, 1897, 30, 833—843).—Although the author can give no method which is absolutely certain for distinguishing between nitramines and nitrosamines, yet, on the whole, Liebermann's nitroso-reaction serves in most cases; Bamberger, also (Abstr, 1893, i, 327; 1894, i, 238; 1895, i, 273), has shown that aromatic nitramines, when treated with mineral acids, yield the corresponding ortho- or paranitranilines, whereas nitrosamines are decomposed by concentrated hydrochloric acid, or, better, by an alcoholic solution of aniline hydrochloride, and the nitroso-group is eliminated. Tolylnitramine, trinitrotolyl- and trinitrophenyl-methylnitramine do not give the nitroso-reaction, not even on warming with phenol. Tolylmethylnitramine gives the nitroso-reaction in the cold, but the colour is not intense and has a greenish tinge. Paranitrophenylnitramine and its methylic salt both in the cold and when heated, orthonitrotolylmethylnitramine in the cold and metanitrotolylnitramine on warming, give bluish-green colorations. Pure dinitrotolylmethylnitramine if heated gives a pure blue coloration, but no colour at all in the cold.

Paratolylmethylnitramine, obtained by the action of sodium methoxide, methylic alcohol, and methylic iodide on paratolylnitramine, crystallises in pale yellow prisms, melts at 74·5—75·5° and is readily soluble in all the usual organic solvents with the exception of cold, light petroleum. When treated with nitric acid, it yields metanitromethylparatoluidine (m. p. 83—84°).

Metanitroparatolylmethylnitramine is a golden-yellow, crystalline compound melting at 106—107° and readily soluble in most solvents, but only sparingly in cold alcohol or ether. It is not converted into dinitromethyltoluidine by the action of dilute acids, even on warning.

Orthonitroparatolylnitramine was obtained from nitrotoluidine by Bamberger's method; it crystallises in nearly colourless needles, melts at 91·5—92·5°, and is readily soluble in most solvents with the exception of water and light petroleum.

Orthonitroparatolylmethylnitramine.—Under this name, the author has previously (Abstr., 1896, i, 161) described a compound which is really a dinitromethyltoluidine. The true nitramine crystallises from alcohol in pale yellow prisms and melts at 82—83°.

Paranitrophenylmethylnitramine crystallises in yellowish needles and melts at 141·5—142·5° (uncorr.).

Trinitrotolylmethylnitramine, $C_6HMe(NO_2)_3{\cdot}NMe{\cdot}NO_2$ [$Me:(NO_2)_3:N = 1:2:3:5:4$], is obtained by the action of fuming nitric acid on orthonitroparatolylmethylnitramine, on nitromethyldimethyltoluidine, or on nitrodimethyltoluidine. It crystallises from its chloroform solution in glistening, yellow needles, melts at 156·5—157° (uncorr.), and is sparingly soluble in ether or light petroleum, but readily in most hot solvents.

Trinitromethyltoluidine was prepared from the above-mentioned trinitro-compound by Romburgh's method; it crystallises in orange-coloured needles, melts at 129·5—130° (uncorr.), and is fairly readily soluble in most solvents. The corresponding *nitrosamine* crystallises in large, yellowish glistening plates and melts at 108—109° (uncorr.). It is readily decomposed even by dilute acids, and gives the Liebermann reaction. This nitrosamine was nitrated in acetic acid solution, the nitroso-group being eliminated. The product was a mixture of two *dinitromethyltoluidines*, which were separated by fractional crystallisation from chloroform and acetone. The one, γ, crystallises in long, orange-coloured plates, melts at 158·5—159·5° (uncorr.), and yields a *nitrosamine* melting at 128—128·5 (uncorr.); the other, β, crystallises in bright red prisms, melts at 184·5—185·5° (uncorr.), and is identical with the product obtained by the action of nitrous acid on orthonitrodimethyltoluidine, or by the oxidation of dinitrodimethyltoluidine (m. p. 104°); it yields a *nitrosamine* melting at 123—124° (uncorr.). Both dinitro-compounds, when further nitrated, yield the trinitrotolylmethylnitramine previously described. The author concludes with a few criticisms on Van Romburgh's work (*Rec. trav. chim.*, 1887, **6**, 365). J. J. S.

Addition of Methylic Iodide to Nitrosodimethylaniline. By Ludwig Knorr (*Ber.*, 1897, **30**, 933—936).—Nitrosodimethylaniline reacts vigorously with methylic iodide to form a *methiodide*, which melts at about 125°. Boiling aqueous soda converts it into the same decomposition products as nitrosodimethylaniline itself, and hence the author concludes that it is probably a pseudomethiodide,

$$NMe_2I⁚C_6H_4⁚N\cdot OMe.$$

A. H.

Acidyl Derivatives of the Nitrosamines. A Contribution to the Diazo-problem. By Julius W. Brühl (*Ber.*, 1897, **30**, 816—821).—The acidyl derivatives of the nitrosamines have been proved to behave in many respects as diazo-compounds (von Pechmann, *Ber.*, 1894, **27**, 703), and the author has now found a striking difference between the refraction equivalents of the group NO in alkyl and acidyl derivatives of the nitrosamines of the fatty series, which seems to indicate that the acidyl derivatives are also in reality diazo-derivatives. The values obtained for the refraction equivalent of the group NO in various nitrosamines of the fatty series are $r_\alpha = 5·33$ and $r_{Na} = 5·37$. The values of the same group in the nitrites, in which it is united with oxygen instead of nitrogen, are only a very little higher; $r_\alpha = 5·86$ and $r_{Na} = 5·91$. The value of the same group in nitrosoethylurethane, $EtO\cdot CO\cdot NEt\cdot N⁚O$ can be obtained by subtracting from the refraction equivalent of this compound that of the residue, $EtO\cdot CO\cdot NEt$– obtained from observations made on ethylurethane. In this way, the numbers are found to be $r_\alpha = 7·05$ and $r_{Na} = 7·07$. The author interprets this result as indicating that, in nitrosoethylurethane, the nitrogen atoms are probably united by multiple linkage, although the exact constitution cannot as yet be ascertained. Many of the reactions of nitrosoethylurethane can be much more simply expressed on this supposition than by means of the older formula. A. H.

Orthonitroparaphenylenediamine. By Carl Bülow and Eugen Mann (*Ber.*, 1897, **30**, 977—988).—With dilute hydrochloric acid, paranitrorthophenylenediamine forms a very stable mon-acid hydrochloride, and with concentrated hydrochloric acid an unstable di-acid compound, the latter being converted into the former on drying at 110—120°; both of these yield a diazo-compound only, and no tetrazo-compound, even when dry nitrous anhydride, N_2O_3, is passed through their alcoholic solutions. On benzoylation, a *monobenzoyl* derivative alone is formed, and similarly on acetylation, the *monacetyl* derivative alone is obtained, the compounds being the same as those produced by nitrating the diacetyl- or dibenzoyl-paraphenylenediamines and partially hydrolysing with alcoholic potash. By nitration, therefore, the nitro-group enters in the same position relatively to the benzoyl amido-group as the benzoyl group to the nitro-group, by the benzoylation of the nitro-base.

Orthonitromonacetylparaphenylenediamine is only a very feeble base, and does not form salts; it readily yields a diazo-compound, however, which, on combination, gives an azo-derivative yielding on hydrolysis a substance structurally isomeric with that produced by combining the diazo-derivative of the base with the same second component. The orthonitrodiacetyl compound, on reduction, yields paradiacetyltriamidobenzene, and this, on treatment with nitrite, passes into *diacetylamidobenzeneazimide*, $NHAc\cdot C_6H_4{<}\genfrac{}{}{0pt}{}{NAc}{N}{>}N$, a substance crystallising from glacial acetic acid in white needles melting at 165°. The corresponding *monacetyl* derivative separates from hot water in greyish-white needles melting at 241°.

All the compounds described have been previously prepared, the above two differing, however, in their melting points from those found by other investigators. J. F. T.

Diazotisation of Aniline. By STEFAN VON NIEMENTOWSKI and JOHANN VON ROSZKOWSKI (*Zeit. physikal. Chem.*, 1897, 22, 145—169). —The authors first determined the solubility and electrical conductivity of the aniline, aniline salts, and nitrites which were subsequently used. Of these, aniline chloride and sulphate are abnormal in their conductivity, giving at $v = 512$ no evidence of the attainment of a final constant value, a result probably due to hydrolytic decomposition. The migration velocity of the $\cdot NO_2$ ion was found to be 72·3, that is, a little higher than that of the nitric acid ion (= 65·1). In aqueous solution, silver nitrite and aniline yield, after many days, a precipitate of diazoamidobenzene and its silver salt, the yield increasing with the dilution. Analogous results were obtained with sodium and potassium nitrites, but the yields were smaller and the reaction slower. The reactions between aniline chloride and sulphate and the three nitrites were studied for different concentrations and proportions. In all cases, the reactions were similar to those represented by the equations

$$(NH_2Ph)_2,H_2SO_4 + AgNO_2 = H_2SO_4 + 2H_2O + Ph\cdot N_2\cdot NAgPh$$

and $(NH_2Ph)_2,H_2SO_4 + AgNO_2 = AgHSO_4 + 2H_2O + Ph\cdot N_2\cdot NHPh$, the first being the chief reaction. The yield was much larger than that obtained from the free base, probably owing to the increased concentration of the $C_6H_5\cdot NH.$ ions. In acid solutions, aniline chloride and sodium nitrite yielded no diazoamidobenzene when the concentration of the acid was double that of the other compounds, whilst with the other nitrites the quantity of this substance formed was greatly reduced by the addition of the second molecule of acid. L. M. J.

Stability of some Diazonium Compounds. By Giuseppe Oddo and G. Ampola (*Gazzetta*, 1896, **26**, ii, 541—548).—Oddo having shown (Abstr., 1895, i, 514) that whilst some diazonium compounds are stable at, and are formed at, higher temperatures, others are formed only at low temperatures, the authors have studied the influence of temperature on the formation of a number of diazonium derivatives; the process adopted was that of dissolving the base (1 mol.) in dilute hydrochloric acid (2 mols.), and after heating to the required temperature, adding concentrated sodium nitrite solution (1 mol.). After cooling and filtering, the quantity of diazonium compound formed was determined by adding alkaline β-naphthol solution or paranitraniline hydrochloride solution to the filtrate.

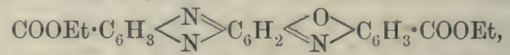
On diazotising at 100—105°, much diazonium compound is formed from meta- and para-nitraniline, parachloraniline, 1 : 3 : 4-dinitraniline and 1 : 2 : 5- and 1 : 3 : 6-nitrotoluidine, whilst little is obtained with meta-, chlor-, and brom-aniline, orthonitraniline, paramidobenzoic acid, and 1 : 5 : 2-nitrotoluidine. At 80—85°, much diazonium compound is obtained with the substances named above as giving little at 100—105°, whilst small yields are obtained with aniline, paratoluidine and α- and β-naphthylamine; at 60—65°, the four bases last named give good yields of diazonium compound, whilst orthotoluidine and paraxylidine give very poor ones. At 40—45°, paraxylidine in turn gives a good yield of diazonium compound.

It is evident from these results that the nature and position of the side chain groups in the base greatly influence the yield of diazonium compound; the presence of acidic radicles promotes the formation of such compounds at high temperatures, whilst that of alkylic radicles has the opposite effect. W. J. P.

Some New Hydroxyazo-compounds, and Derivatives of Triphenodioxazine. By Karl Auwers and H. Röhrig (*Ber.*, 1897, **30**, 988—998).—For cryoscopic purposes, attempts were made to isolate oxyazo-compounds containing strongly negative groups in the para-position relatively to the hydroxyl, and since, as is well known, para-substituted phenols do not readily combine with diazo-chlorides, resort was had to the method of Bamberger and of Mills for the preparation of azo-compounds, namely, combining nitrosobenzene with the corresponding orthamido-derivative of the para-substituted phenol, and in this way many compounds of this class were prepared, although in every case about 20 per cent. of a bye-product was formed, readily separable, however, from the oxyazo-compound, owing to its insolubility in acetic acid; this was found to be a derivative of triphenodioxazine, and was evidently formed by the oxidation of the phenol.

Methylic metanitroparahydroxybenzoate, melting at 75—76°, and the corresponding *ethylic* salt melting at 69°, were first reduced by means of aluminium amalgam to the amido-compounds. *Methylic metamidohydroxybenzoate* crystallises best from benzene, from which it separates in slender needles and leaflets melting at 100—101°; the *ethylic* salt crystallises in glistening, flat prisms from hot chloroform, and melts at 110—111°, whilst the *free acid*, which has already been prepared by other methods, crystallises in light-grey prisms containing $1H_2O$, and when dehydrated melts at 201°.

The condensation of these alkylic salts with nitrosobenzene takes place readily in the presence of acetic acid, forming *ethylic benzeneazoparahydroxybenzoate*, a finely crystalline compound, separating from dilute acetic acid in glistening, orange-red needles melting at 105—106°, and *methylic benzeneazoparahydroxybenzoate*, consisting also of orange-red needles melting at 116—117°; the corresponding *benzeneazohydroxybenzoic acid* crystallises from glacial acetic acid in yellow leaflets melting at 219·5—221°; at the same time, there is also formed *ethylic triphenodioxazinedicarboxylate*,



$$\mathrm{COOEt\cdot C_6H_3}\left\langle\begin{matrix}\mathrm{N}\\\mathrm{N}\end{matrix}\right\rangle\mathrm{C_6H_2}\left\langle\begin{matrix}\mathrm{O}\\\mathrm{N}\end{matrix}\right\rangle\mathrm{C_6H_3\cdot COOEt},$$

an insoluble compound, crystallising from nitrobenzene in dark-red, metallic leaflets and prisms; it dissolves in concentrated sulphuric acid, forming a deep blue solution. The *methylic* salt has precisely similar properties.

Benzeneazoparanitrophenol is produced when nitrosobenzene is allowed to condense with orthamidoparanitrophenol, formed by partially reducing dinitrophenol with ammonium sulphide; it crystallises from dilute acetic acid in orange-red leaflets melting at 150—151°; the *dinitrotriphenodioxazine* formed at the same time can be separated by boiling with glacial acetic acid, and consists of reddish-brown, metallic leaflets, dissolving in concentrated sulphuric acid with a blue-violet coloration.

Orthonitroparacyanobenzene, prepared from metanitroparahydroxybenzaldoxime, crystallises from absolute alcohol in prisms and needles melting at 169°, and passes, on boiling with acetic anhydride, into *acetylmetanitroparahydroxybenzonitrile* (or acetylorthonitroparacyanobenzene), $OAc\cdot C_6H_3(NO_2)\cdot CN$, a compound melting at 113—114°, and yielding, on hydrolysis, *orthonitrocyanophenol*; the latter crystallises from alcohol in yellow leaflets melting at 145°, and on reduction with aluminium amalgam, yields *orthamidoparacyanophenol*; this, when pure, crystallises from hot water in colourless leaflets melting at 157—158°; only traces of the condensation product of this compound with nitrosobenzene could be isolated, it being very unstable. *Dicyanotriphenodioxazine* forms dark-brown, metallic leaflets.

J. F. T.

Constitution of Certain Hydrazones. By Paul C. Freer (*Ber.*, 1897, 30, 736—738. Compare Abstr., 1895, i, 201).—Acetonephenylhydrazone is converted by bromine into acetoneparabromophenylhydrazone hydrobromide, the base of which readily oxidises in the air, forming *parabromobenzeneazoisopropylene*, which crystallises in large, yellow prisms, melts at 33°, and above this temperature decomposes very rapidly. When heated on a platinum spatula, it deflagrates and leaves a voluminous residue of carbon. It is converted by sodium amalgam into the original acetoneparabromophenylhydrazone, and by bromine into a *perbromide*, $C_9H_9N_2Br_6$, which crystallises in yellow rhombohedra, and melts and decomposes at 91°. This is accompanied by a second *perbromide*, $C_9H_9N_2Br_5$, which crystallises in needles, and melts and decomposes at 102°. Both these compounds are converted by sodium amalgam into the bromhydrazone, whilst they are decomposed when boiled with water, with separation of bromine. All these reactions characterise the original compound as an aliphatic azo-derivative.

Acetophenoneparabromophenylhydrazone behaves in a similar manner, yielding by spontaneous oxidation in the air a *substance* which crystallises well, melts and decomposes violently at 48°, and is converted by bromine into a crystalline *perbromide* melting at 180°.

In contrast with these compounds, the substance which is considered by Bender (Abstr., 1888, 53) to be ethylic β-phenylazocrotonate yields no perbromide when treated with bromine, but is converted into resinous products with evolution of hydrogen bromide. A. H.

New Method of Preparing Thiosemicarbazides. By MAX BUSCH and HERM. RIDDER (*Ber.*, 1897, **30**, 843—849).—It has already been shown (Abstr., 1896, i, 581) that phenylthiocarbazinic acid, when heated with aniline at 110°, readily forms diphenylthiosemicarbazide.

1-*Phenyl*-4-*orthotolylsemicarbazide*, $NHPh \cdot NH \cdot CS \cdot NH \cdot C_6H_4Me$, can readily be formed in a similar manner; it crystallises in small, white needles, and melts at 153°.

1-*Phenyl*-4-*dipropylthiosemicarbazide*, $NHPh \cdot NH \cdot CS \cdot NPr_2$, crystallises from light petroleum or from dilute alcohol in glistening needles, melts at 104°, and is readily soluble in the usual solvents with the exception of water.

1-*Phenyl*-4-*diamylthiosemicarbazide* melts at 99—100°, and *phenyldibenzylthiosemicarbazide* at 139°; the latter is but sparingly soluble in light petroleum and in ether.

1 : 4-*Diphenyl*-4-*methylthiosemicarbazide*, $NHPh \cdot NH \cdot CS \cdot NMePh$, melts at 142° and 4-*piperidyl*-1-*phenylthiosemicarbazide* at 120°. Ammonium phenylthiocarbazinate, obtained by passing ammonia into an ethereal solution of the acid, melts at 117·5°, and is readily soluble in alcohol and water. In the preparation of the salt, it is necessary to pass in the ammonia as rapidly as possible, since the acid readily decomposes even in ethereal solution into carbon bisulphide and phenylhydrazine. Phenylthiosemicarbazide could not be obtained by heating the ammonium salt. The method here given cannot be recommended for the preparation of thiosemicarbazides from primary amines, as the yield is too poor (20—25 per cent.), and the compounds can be obtained more readily by means of the thiocarbimides. The method is useful, however, in the case of secondary amines, the thiosemicarbazides of which cannot be prepared by other means. J. J. S.

Formation of Vanillin from Vanillolycarboxylic Acid. By CHARLES GASSMANN (*Compt. rend.*, 1897, **124**, 38).—When 1 part of vanillolycarboxylic acid is boiled with 2 parts of aniline until the disengagement of carbonic anhydride ceases, a compound is formed having the formula $OMe \cdot C_6H_3(OH) \cdot CH \vdots NPh$ [= 3 : 4 : 1], from which vanillin can be separated by heating with 50 per cent. sulphuric acid. From acetylvanilloylcarboxylic acid, by the same method, acetyl vanillin may be obtained. A. C. C.

Action of α-Bromopropionic Chloride on Benzene in presence of Aluminium Chloride. By A. COLLET (*Bull. Soc. Chim.*, 1897, [iii], 15, 715—717. Compare this vol., i, 73).—By the action of aluminium chloride on α-bromopropionic chloride in excess of benzene at 100°, the author obtains the ketone $CHMeBr\cdot COPh$. It is a liquid which boils at 135—137° under 20 mm. pressure, and has a sp. gr. 1·42 at 15°. When oxidised with permanganate, it gives benzoic acid, and when treated with aniline in the cold, the anilide $NHPh\cdot CHMe\cdot COPh$ is obtained in crystals melting at 98°. The anilide of the bromopropiophenone, obtained by Pampel and Schmidt by direct bromination of propiophenone, melts at 38°. M. W. T.

Action of Acetic Chloride and Benzoic Chloride on Styrene in presence of Zinc Chloride. By ISSAR TAGER (*Chem. Centr.*, 1896, ii, 354, from *Diss. Dorpat*, 1896).—*β-Chlorobenzoylacetone* and *benzylideneacetone* are formed by the action of acetic chloride on styrene in presence of zinc chloride. The hydrazone of the former is crystalline but very unstable, decomposing very easily into substances which give the pyrazolone reaction. By the action of hydrochloric acid, it breaks down into acetone, benzaldehyde, and phenylhydrazine. Benzylideneacetone gives a hydrazone, which at the moment of formation probably changes into a pyrazolone. β-Chlorobenzoylacetone forms a crystalline oxime, benzylideneacetone a liquid oxime which unites with bromine to form a crystalline substance. By treating a mixture of both ketones with moist silver oxide, a ketonic alcohol is obtained.

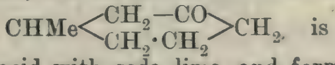
Benzoic chloride reacts with styrene in a similar way to acetic chloride. E. W. W.

Electrolysis of Benzoic Acid. By WALTHER LÖB (*Zeit. Elektrochem.*, 1896, 3, 3).—A somewhat alkaline solution of sodium benzoate is electrolysed with a current density of 0·209 ampère per sq. cm. at the cathode and 0·151 at the anode, the temperature not exceeding 40°. After decomposition of the greater part of the benzoic acid, it is possible to isolate from the solution a substance having the composition $C_5H_5NaO_6$ which crystallises in large plates. It softens at 240°, but is not liquid at 285°, dissolves readily in water, alcohol, glacial acetic acid, soda, or dilute acids, sparingly in amylic alcohol, ether, benzene, light petroleum, chloroform, ethylic acetate, and fuming hydrochloric acid. In concentrated sulphuric acid, it dissolves without coloration. The aqueous solution gives no precipitates with metallic salts. Iodine does not attack it at 180—190°, but bromine reacts with it, yielding a product melting at 181°, the yield of this substance being about 1 per cent. of the benzoic acid used. The gases evolved during the electrolysis consist of carbonic anhydride, carbonic oxide, and small quantities of acetylene. A small but easily recognised quantity of benzaldehyde is formed, but neither aromatic hydrocarbons nor fatty acids could be detected. T. E.

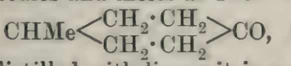
Reduction of Phenolcarboxylic Acids. By ALFRED EINHORN (*Annalen*, 1897, 295, 173—187. Compare Abstr., 1896, i, 45 and 530). —The cresotic acids have been included in the experiments dealing with the behaviour of phenolcarboxylic acids towards sodium and amylic alcohol; the ortho-, meta-, and para-compounds yield α-, β-, and γ-methylpimelic acids respectively. Employment of the acids themselves, however, results in the production of a very small yield; this difficulty is overcome by reducing brominated cresotic acids, an artifice which raises the yield to 70 per cent. of that required by theory.

[With HERMANN EHRET].—α-Methylpimelic is produced in small quantity when orthocresotic acid is reduced with sodium and amylic alcohol; it is more convenient, however, to reduce *dibromorthocresotic acid,* which crystallises from dilute alcohol in white needles resembling ammonium chloride, and melts at 232°. α-Methylpimelic acid, which has been already described by Zelinsky and Generosoff (Abstr., 1896, i, 350), is also obtained on reducing α-hydroxyuvitic acid. The *calcium* salt is a white precipitate formed on adding alcohol to the aqueous solution; the *diethylic* salt boils at 132—137° under a pressure of 23 mm., and the *anilide* crystallises from dilute alcohol in lustrous, white needles melting at 166—167°.

Dibromometacresotic acid cystallises from dilute alcohol in white needles, and melts at 234°; reduction with sodium and amylic alcohol converts it into *β-methylpimelic acid,* $COOH{\cdot}CH_2{\cdot}CHMe{\cdot}[CH_2]_3{\cdot}COOH$, which melts at 48—50°, and distils without undergoing change. The *calcium* salt crystallises in leaflets; the *diethylic* salt boils at 155—160° under a pressure of 25 mm., and the *anilide* melts at 136°.

β-Methylcyclohexanone,  $CHMe{<}\begin{matrix}CH_2{-}CO\\CH_2{\cdot}CH_2\end{matrix}{>}CH_2$, is obtained by heating β-methylpimelic acid with soda lime, and forms a colourless liquid having a faint odour of peppermint; it boils at 162—164°, and is not identical with the cyclic ketone obtained by Wallach on heating pulegone with anhydrous formic acid (Abstr., 1896, i, 309). The *semicarbazone* melts at 191—192°, and the *dibenzylidene* derivative crystallises from methylic alcohol in yellow needles, and melts at 121—122°. The author regards the synthetical product as the racemic modification of the ketone, β-methylcyclohexanone from pulegone being the dextrogyrate form.

Dibromoparacresotic acid crystallises from dilute alcohol in prismatic needles, and melts at 204—205°; reduction converts it into *γ-methylpimelic acid,* $CHMe(CH_2{\cdot}CH_2{\cdot}COOH)_2$, which melts at 56—57° and distils without decomposing. The *calcium* salt is precipitated from the aqueous solution by alcohol, the *diethylic* salt boils at 160—167° under a pressure of 31 mm., and the *anilide* crystallises from dilute alcohol in silky, white needles and melts at 158—159°.

γ-Methylcyclohexanone,  $CHMe{<}\begin{matrix}CH_2{\cdot}CH_2\\CH_2{\cdot}CH_2\end{matrix}{>}CO$, is obtained when γ-methylpimelic acid is distilled with lime; it is a colourless oil, which boils at 163—165°, and forms a crystalline compound with sodium hydrogen sulphite. The *semicarbazone* melts at 199°. M. O. F.

Hexahydroanthranilic Acid. By ALFRED EINHORN (*Annalen,* 1897, **295**, 187—222. Compare Einhorn and Meyenberg, Abstr., 1894, i, 591).—[With BENJAMIN S. BULL and ALFRED GERNSHEIM.]—*Orthourethanehexahydrobenzoic acid,* $COOH{\cdot}C_6H_{10}{\cdot}NH{\cdot}COOEt$, obtained by agitating an aqueous solution of sodium hexahydroanthranilate with ethylic chlorocarbonate, crystallises from ethylic acetate in colourless needles melting at 158·5°; the *ethylic* salt forms needles, and melts at 59—60°.

Benzoylhexahydroanthranilic acid, $COOH\cdot C_6H_{10}\cdot NHBz$, crystallises from dilute alcohol in colourless needles, and melts at 220—221°; the *ethylic* salt melts at 131°. *Ethylic benzenesulphonehexahydroanthranilate*, $COOEt\cdot C_6H_{10}\cdot NH\cdot SO_2Ph$, is obtained by the action of benzenesulphonic chloride on ethylic hexahydroanthranilate, and crystallises from a mixture of benzene and petroleum in white prisms melting at 93°.

[With B. S. BULL.]—When ethylic hexahydroanthranilate is exposed to air, it becomes converted into the acid in a few days; the *platinochloride* of the salt crystallises in orange-coloured scales, and explodes at 219—220°.

Orthoparadinitrophenylhexahydrophenylamineorthocarboxylic acid,

$$C_6H_3(NO_2)_2\cdot NH\cdot C_6H_{10}\cdot COOH,$$

is obtained by heating hexahydroanthranilic acid, dinitrochlorobenzene, and potassium carbonate with dilute alcohol in a reflux apparatus until a portion of the liquid dissolves completely in alkali after removing the alcohol; it forms orange-coloured crystals, and melts at 241°. The *ethylic* salt crystallises in greenish-yellow needles, and melts at 136—137°.

Ethylic orthophenylthiouraminohexahydrobenzoate,

$$NHPh\cdot CS\cdot NH\cdot C_6H_{10}\cdot COOEt,$$

produced on adding phenylcarbimide to a solution of ethylic hexahydroanthranilate in acetone, crystallises from a mixture of acetone and petroleum in microscopic needles melting at 162—163°.

Ethylic orthothiocarbamidehexahydrobenzoate,

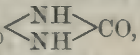
$$CS(NH\cdot C_6H_{10}\cdot COOEt)_2,$$

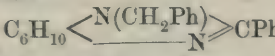
is obtained by heating ethylic hexahydroanthranilate with carbon bisulphide and absolute alcohol in a reflux apparatus on the water bath, and crystallises from 80 per cent. alcohol in white needles melting at 133°.

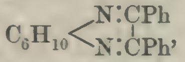
Hexahydroanthranilamide, $NH_2\cdot C_6H_{10}\cdot CONH_2$, is not prepared by the action of phosphorus pentachloride on hexahydroanthranilic acid and subsequent treatment with ammonia, but from ethylic hexahydroanthranilate by acting on it with methylic alcoholic ammonia in sealed tubes at 145° during 7 hours; it crystallises from absolute alcohol in slender needles, and melts at 153·5°. The *platinochloride* forms pale orange crystals, and explodes at 234—237°; the *hydrochloride* and *hydrobromide* crystallise from absolute alcohol in prismatic needles, and melt at 251—252° and 257—259° respectively.

The compound, $C_7H_{12}N_2O$, obtained by the action of alkali hypobromite on the amide (Abstr., 1896, i, 472) forms a *nitroso*-derivative, which is precipitated from chloroform by petroleum, and explodes at 65°; the *benzoyl* derivative crystallises in small, slender needles, and melts at 187°.

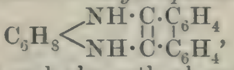
Hexahydro-orthophenylenediamine (orthohexamethylenediamine) is obtained from the intermediate compound, $C_7H_{12}N_2O$, by the action of hot, concentrated hydrochloric acid; it is an oily liquid of ammoniacal odour, absorbs atmospheric carbonic anhydride, solidifies in a freezing mixture, and boils at 183—185° under a pressure of 720 mm. The dihydrochloride (*loc. cit.*) crystallises on adding ethylic acetate to the solution in dilute alcohol, and does not melt below 280°; the *dihydrobromide* behaves in the same way, whilst the *hydrobromide* crystallises from absolute alcohol in small plates, and melts at 209—214°. The *platinochloride* is pale yellow, and the *picrate* forms small, yellow needles, becoming black between 210° and 250°; the *carbamate* separates as a white powder when carbonic anhydride is passed into an ethereal solution of the base, and sublimes at 170—178°. The *diacetyl* derivative sublimes without decomposing, and melts at 260—261°, whilst the *dibenzoyl* derivative crystallises from glacial acetic acid in needles, and does not melt below 280°; the *dibenzenesulphonic* derivative melts at 155°.

Hexahydro-orthophenylenecarbamide,  $C_6H_{10}{<}\begin{matrix}NH\\NH\end{matrix}{>}CO$, is produced when phosgene is passed into a solution of hexahydro-orthophenylenediamine in excess of caustic soda; it crystallises from ethylic acetate in quadratic plates or prisms, reduces Fehling's solution, sublimes without decomposing, and melts at 230—231°.

μ-Phenylhexahydrobenzylbenzimidazole,  $C_6H_{10}{<}\begin{matrix}N(CH_2Ph)\\ \overline{\qquad\quad}N\end{matrix}{\geqslant}CPh$, is obtained on adding benzaldehyde (2 mols.) to a solution of hexahydro-orthophenylenediamine which has been neutralised with sodium carbonate; it crystallises from alcohol in short, white needles, and melts at 132·5°.

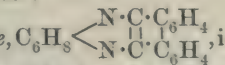
B-*Hexahydro-aβ-diphenylquinoxaline*,  $C_6H_{10}{<}\begin{matrix}N{:}CPh\\ \quad | \\ N{:}CPh\end{matrix}$, prepared by heating hexahydro-orthophenylenediamine with an alcoholic solution of benzil (1 mol.) on the water bath, crystallises in sulphur-yellow, prismatic needles melting at 167—169°, and distilling without change; concentrated hydrochloric and sulphuric acids dissolve it with development of a red coloration, and water precipitates benzil from the solutions. The quinoxaline derivative is also produced from hexahydro-orthophenylenediamine and benzoin, and in this respect affords a parallel with aβ-diphenyl-γδ-dihydropyrazine, which is the product of the action of ethylenediamine alike on benzil and benzoin.

B-*Tetrahydro-aβ-phenanthra-n-dihydroquinoxaline*,



$$C_6H_8{<}\begin{matrix}NH\cdot C\cdot C_6H_4\\ \quad\ \ \| \quad | \\ NH\cdot C\cdot C_6H_4\end{matrix},$$

is obtained by heating hexahydro-orthophenylenediamine with phenanthraquinone (1 mol.) dissolved in methylic alcohol, and crystallises in orange needles, melting at 145·5°; the solution in concentrated hydrochloric or sulphuric acid is green. The *monacetyl* derivative becomes red at 140°, and melts at 163—165°.

B-*Tetrahydro-aβ-phenanthraquinoxaline*,  $C_6H_8{<}\begin{matrix}N\cdot C\cdot C_6H_4\\ \quad \| \quad | \\ N\cdot C\cdot C_6H_4\end{matrix}$, is produced when the foregoing compound is heated with glacial acetic or mineral acids, and crystallises in pale yellow needles, melting at 202—204°; the solution in concentrated sulphuric acid is brownish-red. M. O. F.

Action of Ethyloxalic Chloride [Ethylic Chloroglyoxylate] on ψ-Cumene and on Mesitylene. By E. (? LOUIS) BOUVEAULT

(*Compt. rend.*, 1897, 124, 156—158. Compare Abstr., 1896, i, 551, 616, 649, 650).—ψ-Cumene readily reacts with ethylic chloroglyoxylate in presence of aluminium chloride, forming *ethylic ψ-cumylglyoxylate*, a yellow liquid of disagreeable odour, and boiling at 175°—176° (10 mm.). ψ-Cumylglyoxylic acid separates from carbon bisulphide in colourless crystals melting at 76°, and is identical with the acid obtained by Claus by the oxidation of acetyl-ψ-cumene. When its solution in concentrated sulphuric acid is poured into water, durylic acid is obtained. When heated with aniline, it gives a yellow crystalline *phenylimide* boiling at 206° (10 mm.) and melting at 62°. When boiled with dilute sulphuric acid, this phenylimide yields the corresponding *aldehyde*, $C_6H_2Me_3{\cdot}COH$, which forms colourless crystals melting at 43·5° and boiling at 121° (10 mm.); from this, the *hydrazone*, $N_2(\colon CH{\cdot}C_6H_2Me_3)_2$, melting at 181° and soluble in benzene and light petroleum, is obtained. In the action of ethylic chloroglyoxylate on ψ-cumene, no isomerides of ψ-cumylglyoxylic acid are formed. Ethylic mesitylglyoxylate is obtained in a similar manner to the corresponding ψ-cumene derivative as a yellow liquid boiling at 164—165° (11 mm.); the corresponding acid, crystallised from carbon bisulphide, melts at 117—118°, and is identical with the acid obtained by Claus. When heated at 100° with a solution of hydrazine hydrate, it yields the *acid*, $N_2[\colon C(C_6H_2Me_3){\cdot}COOH]_2 + H_2O$, melting at 200° and giving rise, with loss of carbonic anhydride, to the hydrazone of the corresponding aldehyde. The *phenylimide* forms yellow crystals melting at 48—49°, boiling at 202° (10 mm.), and is converted by dilute sulphuric acid into the corresponding aldehyde melting at 14° and boiling at 117° (10 mm.), which has already been described by Feith (Abstr., 1892, 329), who only obtained it as a liquid. Its hydrazone forms yellow crystals melting at 171°, and is almost insoluble in ether, but fairly soluble in hot benzene.

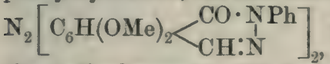
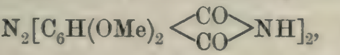
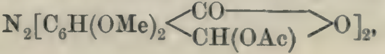
Acetylmesitylene does not react with hydrazine hydrate.

A. C. C.

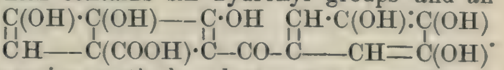
Nitrophenoxy-acids. By ATTILIO PURGOTTI (*Gazzetta*, 1896, 26, ii, 554—559).—Although sodium chloracetate reacts with sodionitrophenol, giving a nitrophenoxyacetic acid, it does not react with picric chloride, and attempts which the author has made to bring about a similar reaction between picric chloride and the ethylic sodioglycolate or ethylic lactate were unsuccessful. Picric chloride, however, reacts with methylic sodiosalicylate in boiling toluene solution giving *methylic picrylsalicylate*, $C_6H_2(NO_2)_3{\cdot}O{\cdot}C_6H_4{\cdot}COOMe$, which forms yellow crystals melting at about 139°; attempts to obtain the free acid were unsuccessful, as when hydrolysis occurs picric and salicylic acids are formed.

Picrylsalicylaldehyde, $C_6H_2(NO_2)_3{\cdot}O{\cdot}C_6H_4{\cdot}COH$, is obtained by boiling salicylaldehyde and picric chloride with soda in alcoholic solution; it forms small, yellow crystals melting at 154°, and is readily converted into a *phenylhydrazone*, $C_6H_2(NO_2)_3{\cdot}O{\cdot}C_6H_4{\cdot}CH\colon N{\cdot}NHPh$, which crystallises in yellow needles melting at 217°. W. J. P.

Azo-opianic Acid. By ADOLPH CLAUS and FRANZ PREDARI (*J. pr. Chem.*, 1897, [ii], 55, 171—185).—The substance that is still often

described under this name, for example, in the third edition of Beilstein's *Handbuch*, and is obtained by the reduction of nitro-opianic acid with stannous chloride, has long been shown to be in reality an anhydride (resembling anthranil in character) of orthamidohemipinic acid. The true *azo-opianic acid*,
$N_2[C_6H(OMe)_2(CHO)\cdot COOH]_2$ [N:(OMe)$_2$:COOH:CHO = 1:3:4:5:6] is obtained by reducing nitro-opianic acid in aqueous solution with 2½ per cent. sodium amalgam at 0°. It is yellow, and melts and decomposes at 174°; the salts are yellow to brown in colour, and the *sodium*, $C_{20}H_{16}N_2O_{10}Na_2 + 3H_2O$; *potassium*, $C_{20}H_{16}N_2O_{10}K_2 + 6H_2O$, and *barium* salts are very soluble in water, whilst the *copper*, *iron*, *lead*, $C_{20}H_{16}N_2O_{10}Pb$, and *silver* salts form flocculent precipitates. With phenylhydrazine, the acid condenses to red *azo-opianic-phenylhydrazide*,  $N_2\left[C_6H(OMe)_2{<}\begin{array}{l}CO\cdot NPh\\ \quad\;\, | \\ CH:N\end{array}\right]_2$, melting at 258°, which is at the same time a hydrazone; with hydroxylamine, it yields yellow *azohemipinimide*  $N_2[C_6H(OMe)_2{<}\begin{array}{l}CO\\CO\end{array}{>}NH]_2$, melting and decomposing at 250°; with acetic anhydride and sodium acetate, it yields yellow *azo-opianic anhydroacetate*,  $N_2[C_6H(OMe)_2{<}\begin{array}{l}CO\text{———}\\CH(OAc)\end{array}{>}O]_2$, melting at 210°.

When azo-opianic acid (1 mol.) is suspended in a little water, or dissolved in a little acetic acid, and then boiled with fuming nitric acid (1 mol.), a reddish, crystalline substance is obtained which is still unmelted at 280°, and apparently has the composition $C_{20}H_{15}N_3O_9$. When the acid is heated with strong hydrochloric acid, a colourless, crystalline substance is obtained which does not melt at 300°, and appears to have the composition $C_{10}H_9NO_5$. C. F. B.

Constitution of Tannic Acid. By HUGO SCHIFF (*Gazzetta*, 1897, 27, i, 90—96).—The author having shown that the natural tannic acid is dextrorotatory (Abstr., 1896, i, 370), suggested for it the following constitution, which contains six hydroxyl groups and an asymmetric carbon atom,  $\begin{array}{l}C(OH)\cdot C(OH)\text{——}C\cdot OH\quad CH\cdot C(OH):C(OH)\\ \|\qquad\quad |\qquad\quad\;\; \|\qquad\;\; \|\qquad\qquad\qquad\quad |\\ CH\text{——}C(COOH)\cdot C\text{–}CO\text{–}C\text{——}CH{=}C(OH)\end{array}$. On acetylating the acid by various methods, a dextrorotatory *pentacetyltannic acid* is obtained which is insoluble in water, and has about the same specific rotation as natural tannic acid; the compositions of the cupric, ammoniocupric, lead, and mercuramine salts (Abstr., 1875, 1197) also point to the existence of only five hydroxyl groups in tannic acid.

Gallic acid gives a good yield of rufigallol when heated with concentrated sulphuric acid at 100°, and if the ketonic nature of tannic acid as expressed by the above constitution is correct, the latter acid should yield rufigallol with even greater readiness. On heating tannic acid with concentrated sulphuric acid at 100°, however, carbonisation occurs and sulphurous anhydride is evolved; a little rufigallol is indeed formed, but only from the gallic acid into which the tannic acid is partially converted. Tannic acid gives no hydrazone, but only a resinous substance when treated with phenylhydrazine under various conditions.

The author was unable to synthesize tannic acid by B. Hunt's method (Abstr., 1885, 1228) of heating bromoprotocatechuic acid with potassium gallate and a little alcohol or water at 100—105°; this synthesis, therefore, cannot be used in support of the older formula for tannic acid which contains no asymmetric carbon atom.

W. J. P.

Some Ethylic Salts of Phthalic and Tetrachlorophthalic Acid. By Richard E. Meyer and A. Jugilewitsch (*Ber.*, 1897, **30**, 780—788).—The object of these experiments was to determine whether the ethylic salts obtained by the action of alkylic iodides on silver phthalate were isomeric or identical with these formed by the action of the corresponding alcohol on phthalic chloride, and thus to indicate the symmetrical or asymmetrical structure of the latter. In every case examined, the two compounds were found to be identical.

Benzylic phthalate crystallises from alcohol in thick prisms, melting at 42—43°, the *benzylic hydrogen salt* melting at 102—104°.

Paranitrobenzylic phthalate separates from benzene in long needles melting at 154—155°.

Cetylic phthalate crystallises from alcohol in slender needles melting at 42—43°.

Benzylic tetrachlorophthalate crystallises from methylic alcohol in colourless needles melting at 92—93°.

Paranitrobenzylic tetrachlorophthalate separates from hot benzene in long needles melting at 179—180°, whilst *cetylic tetrachlorophthalate* is precipitated from its ethylic acetate solution by means of methylic alcohol as fine leaflets melting at 49—50°.

J. F. T.

Addition of Halogens and Halogen Acids to Unsaturated Sulphones. By Julius Troeger and A. Hinze (*J. pr. Chem.*, 1897, [ii], **55**, 202—217).—The unsaturated sulphones were of the type $R\cdot SO_2\cdot CH_2\cdot CH{:}CH_2$, and were obtained by the action of allylic bromide on sulphinates. Either alone or in solution in carbon tetrachloride, they readily absorb chlorine, forming dichlorides, and, when dissolved in glacial acetic acid, they unite with bromine, yielding dibromides, but they will not unite with iodine. They also unite with hydrogen bromide or iodide, yielding compounds $R\cdot SO_2\cdot CH_2\cdot CHX\cdot CH_3$ when heated for several hours with a solution of the gas in glacial acetic acid, at 120° and 140° respectively; with hydrogen chloride, they will not unite, even at 200°. It is already known that heating these dibromides with water for 20—40 hours at 120—140° sometimes leads to the formation of a glycol, but, in the case of β-naphthylallylsulphone dibromide, to the replacement of the two atoms of bromine by one of oxygen; the α-naphthyl isomeride is now found to behave like the β-compound, whereas paratolylallylsulphone dibromide yields a glycol. The new compounds described are enumerated below, and their melting points given.

Phenylallylsulphone dichloride, 72—73°. *Paratolylallylsulphone dichloride*, 78—79°. *Naphthylallylsulphone dichlorides*; α, oil; β, between 103° and 110°. *α-Naphthylallylsulphone dibromide*, oil. *Monobromo-*

propylphenylsulphone, *monobromopropylparatolylsulphone*, *monobromopropyl-a-naphthylsulphone*, the corresponding iodo-compounds, and also moniodopropylorthotolylsulphone are all oils. Paratolylpropyleneglycol, $C_6H_4Me\cdot SO_2\cdot C_3H_5(OH)_2$, 93—95°. *a-Naphthyl compound*, $C_{10}H_7\cdot SO_2\cdot C_3H_5O$, 127°.

Benzylsulphamic Acid and Derivatives of Benzylsulphonitrosamic Acid. By Carl Paal and Leopold Lowitsch (*Ber.*, 1897, **30**, 869—879).—In former papers (Paal and Kretschmer, Abstr., 1894, i, 365; Paal and Jänicke, Abstr., 1896, i, 235), it was shown that primary aromatic amines and hydrazines combine with amidosulphonic acid with the formation of the ammonium salts of sulphamic and hydrazidosulphonic acids, and it was further stated that fatty amines do not react quite in the same way, isoamylamine, for instance, forming the amylamine compound of isoamylsulphamic acid, $C_5H_{11}\cdot NH\cdot SO_3H,NH_2\cdot C_5H_{11}$. It therefore seemed interesting to study the behaviour of aromatic amines of the type of benzylamine under similar conditions. On boiling benzylamine with excess of amidosulphonic acid in alcoholic solution, the *benzylamine amidosulphonate*, $NH_2\cdot SO_3H,NH_2\cdot C_7H_7$, is alone produced, and only on heating the mixture in a closed tube at 200° does rearrangement take place, with the formation of *benzylamine benzylsulphamate*,

$$CH_2Ph\cdot NH\cdot SO_3H,NH_2\cdot C_7H_7.$$

The former compound forms white, glistening leaflets melting at 121°, and the latter long prisms melting at 179°.

On hydrolysing this benzylamine compound by means of hydrochloric acid, the corresponding *benzylsulphamic acid*, $CH_2Ph\cdot NH\cdot SO_3H$, is produced as a well defined crystalline substance forming long, white needles melting with decomposition at 194°, the *barium* salt forms colourless, transparent plates free from water of crystallisation, and the *silver* salt white needles, stable in the light, and very soluble in water.

On treating benzylsulphamic acid with potassium nitrite, *potassium benzylsulphonitrosamate*, $C_7H_7\cdot N(NO)\cdot SO_3K$, is produced, the corresponding compound being formed with sodium nitrite, and although the free acid does not seem capable of existence, yet these salts readily combine with the hydrochlorides of organic bases, with formation of the amine salts of benzylsulphonitrosamic acid, thus the *isoamylamine* salt forms fine, white leaflets, decomposing at ordinary temperatures; the *aniline* salt, white needles, exploding on touching; the *phenylhydrazine* compound slender, white needles, also very explosive; the *paratoluidine* salt, white needles, very soluble in alcohol, and explosive even in the moist condition; and the *a-naphthylamine* salt, faintly red leaflets, which explode violently on scratching with a sharp piece of glass.

In many respects, the salts of benzylsulphonitrosamic acid show a remarkable resemblance to the diazo-compounds, thus on boiling with water, nitrogen is eliminated and benzylic alcohol produced, with halogen acids the corresponding benzylic haloid is formed, whilst ethylic alcohol gives rise to benzylic ethylic ether.

The product formed when a-naphthylamine benzylsulphonitrosamate explodes is an azo-dye, namely, the hydrochloride of *benzyl-*

azo-a-benzylnaphthylamine, $CH_2Ph\cdot N_2\cdot C_{10}H_6\cdot NH\cdot C_7H_7,HCl$, a substance crystallising from its beautifully blue solutions in small, dark blue needles, melting and decomposing at 224°; the *base* crystallises from ether in red needles. J. F. T.

Derivatives of Paratolylsulphnitrosamic Acid. By CARL PAAL and S. DEYBECK (*Ber.*, 1897, **30**, 880—887. Compare preceding abstract).—*Paratolylsulphamic acid*, on treatment with sodium nitrite, yields sodium *paratolylsulphonitrosamate*, $C_6H_4Me\cdot N(NO)\cdot SO_3Na$, a white, crystalline salt decomposing on heating, and similar in its behaviour to the sodium benzyl-sulphonitrosamate previously described, yielding, as it does, with water, paracresol; with ethylic alcohol, paratolyl ethyl ether, and with hydrogen iodide, paraiodotoluene. With β-naphthol, it yields *paratolyl β-naphthyl ether*, $C_6H_4Me\cdot O\cdot C_{10}H_7$, a red compound crystallising from dilute alcohol in needles melting at 135°, and with α-naphthylamine hydrochloride, *paratolylazo-α-naphthylamine*, $C_6H_4Me\cdot N\colon N\cdot C_{10}H_6\cdot NH_2$, the *hydrochloride* of which crystallises from dilute alcohol containing hydrogen chloride, in blue black needles melting at 162—164°.

In the action of nitro-sulphuric acid on potassium paratolylnitrosamate, potassium *paratolylsulphonitramate*, $C_6H_4MeN(NO_2)\cdot SO_3K$, is formed as the chief product. J. F. T.

Metatoluenesulphonic Acid. By JOHN J. GRIFFIN (*Amer. Chem. J.*, 1897, **19**, 183—199).—An historical sketch of the work done on the isomeric toluenesulphonic acids is given. To prepare metatoluenesulphonic acid, metatoluenesulphonamide is heated with hydrochloric acid in sealed tubes at 140° for 6 hours, cooled, and the ammonium chloride which separates filtered off; the solution is boiled with potassium hydroxide until there is no longer any odour of ammonia, the solution evaporated to dryness, and extracted with alcohol, when the potassium salt of metatoluenesulphonic acid is obtained in minute scales. When treated with phosphorus pentachloride, the latter yields the sulphonic chloride, and this by treatment with water gives the free acid, which remains liquid at a temperature of −18°. The *barium*, *lead*, *calcium*, *sodium*, *potassium*, *silver*, *magnesium*, *manganese*, *zinc*, and *copper* salts are described.

Metatoluenesulphonanilide, formed from aniline and metatoluenesulphonic chloride, crystallises from alcohol in large, monoclinic prisms, and from ether in small, prismatic crystals, melting at 72°.

Metatoluenesulphonorthotoluidide is formed from the sulphonic chloride and orthotoluidine; it crystallises in prisms and thick plates, melts at 108°, and is insoluble in water but readily soluble in ether, alcohol, and benzene.

Metatoluenesulphonparatoluidide prepared in a similar manner crystallises in small prisms, and melts at 106°. A. W. C.

Action of Ethylic and Methylic Alcohols on Paradiazometatoluenesulphonic Acid in the presence of Various Substances. By JOHN J. GRIFFIN (*Amer. Chem. J.*, 1897, **19**, 163—183).—Paradiazometatoluenesulphonic acid, prepared by diazotising paratoluidinemetasulphonic acid, was submitted to the action of alcohol in presence of various substances, in order to determine whether the diazo-group is replaced by hydrogen or an ethoxy-group.

When the diazo-compound is acted on by methylic alcohol in presence of sodium methoxide, a hard, pale brown substance is produced, which, on treatment with phosphorus pentachloride and ammonia, is converted into metatoluenesulphonamide.

The same result is obtained if the sodium methoxide is replaced by sodium carbonate, sodium hydroxide, or zinc dust, or when ethylic alcohol is used instead of methylic alcohol. In the latter case, the yield of the amide is smaller. With methylic alcohol and calcium carbonate, no reaction takes place.

The product of the action of methylic alcohol and ammonia on the diazo-compound is the ammonium salt of paratoluidinemetasulphonic acid, which was proved by diazotising, decomposing with methylic alcohol and caustic soda, and treating the resulting substance with phosphorus pentachloride and ammonia, when metatoluenesulphonamide was again produced.

The best yield of the amide is obtained by treating the product obtained by the action of methylic alcohol and zinc dust in the diazo-compound with phosphorus trichloride (instead of the pentachloride) and ammonia.

Metatoluenesulphonamide melts at 108°, crystallises from water in brilliant hexagonal scales or large, fern-like growths, according to the concentration of the solution, and from alcohol in monoclinic prisms.

Metasulphaminebenzoic acid is produced when metatoluenesulphonamide is oxidised with sulphuric acid and potassium dichromate. It melts at 223° (uncorr.), and volatilises on gentle heating. When heated at 245—250° for 45 minutes and then cooled, it sets to a brown, vitreous mass, easily soluble in cold water, from which it crystallises in needles on evaporation.

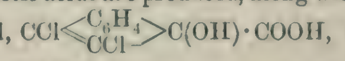
Barium and silver salts of the acid are described. The latter contains no water of crystallisation, which is contrary to what has been previously stated to be the case. A. W. C.

Condensation of Hydrols with Aromatic Amines in Presence of Sulphuric Acid. By MAURICE PRUD'HOMME (*Bull. Soc. Chim.*, 1897, [iii], **15**, 717—720).—Nölting has shown that when aromatic amines, such as paratoluidine, condense with tetramethyldiamidobenzhydrol in presence of strong sulphuric acid, the leuco-bases of blue-green dyes are produced. In presence of hydrochloric acid, the products are leuco-bases of pure green dyes, replacement in the paratoluidine molecule taking place respectively in the ortho- and meta-positions with regard to the amido-group.

The author compares the condensation of other benzhydrol derivatives with aromatic bases; he concludes that in sulphuric acid solution replacement in the amine takes place chiefly in the para-position, if the para-position is free, with the formation of violet-blue dyes. Replacement may, at the same time, take place in the ortho- or para-position, with formation of green dyes. M. W. T.

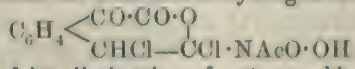
Benzyl Derivatives of Pararosaniline. By MAURICE PRUD'HOMME (*Bull. Soc. Chim.*, 1897, [iii], **15**, 720—723).—The author has prepared a large number of the benzene derivatives of pararosaniline; he finds that the change of colour produced by the entry of a benzyl group into the molecule is practically equivalent to that produced by the introduction of a methyl group, the phenyl group having little influence when attached to a side chain. M. W. T.

Action of Acid Chlorides on Methoxynaphthol in presence of Aluminium Chloride. By L. Rousset (*Bull. Soc. Chim.*, 1896, [iii], 15, 633—638).—A solution containing butyric chloride and α-methoxynaphthalene in molecular proportion is added, in small quantities at a time, to a flask containing aluminium chloride and carbon bisulphide, hydrogen chloride is given off, and a mixture of three isomeric *α-methoxynaphthyl propyl ketones* is obtained. By recrystallisation from alcohol, a compound, which probably corresponds with the formula $OMe\cdot C_{10}H_6\cdot COPr$ [= 1 : 4] is separated. This appears to be the chief product of the reaction; it melts at 49—50°, and forms a red, crystalline picrate which melts at 90° (compare this vol., i, 75). From the mother liquor, by the picric acid method already described, two isomeric ketones can be separated; one, a liquid, boils at 212—217° under 18 mm. pressure, and does not form a crystalline picrate; the other, a crystalline solid, melts at 33—34°, and forms a picrate which melts at 103—104°. By the action of acetic chloride on β-methoxynaphthalene, a large quantity of a ketone, $OMe\cdot C_{10}H_6\cdot COMe$, is obtained; this melts at 57°, boils at 205° under 22 mm. pressure, and is identical with the compound described by Gattermann. From the mother liquor, a small quantity of a liquid isomeride is obtained. M. W. T.

Conversion of Nitro-β-naphthaquinone into Indene Derivatives. By E. G. Theodor Zincke (*Annalen*, 1897, **295**, 1—6. Compare Abstr., 1892, 1229).—Orthodichloronitroethylbenzoylcarboxylic acid, obtained by the action of chlorine on nitro-β-naphthaquinone, is converted by acetic chloride into an acetyl derivative which is devoid of acidic properties, and yields a dirty, flocculent substance when treated with warm, dilute soda (*loc. cit.*); nitrous acid is produced in the change, although no trace of this substance is eliminated when the original compound is treated with hot alkali. If the action of alkali on the acetyl derivative is conducted at the ordinary temperature, nitrous and acetic acids are produced, along with dichlorindenehydroxycarboxylic acid,  $CCl{<}\begin{smallmatrix}C_6H_4\\ CCl\end{smallmatrix}{>}C(OH)\cdot COOH$, which is recognised by oxidising it to dichlorindone.

The author explains this change by regarding dichloronitroethylbenzoylcarboxylic acid as acting towards acetic chloride in conformity with the structure $COOH\cdot CO\cdot C_6H_4\cdot CHCl\cdot CCl{:}NO\cdot OH$, giving rise to the unstable additive compound,

$$COOH\cdot CO\cdot C_6H_4\cdot CHCl\cdot CCl_2\cdot NAcO\cdot OH,$$

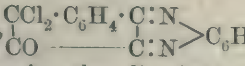
which loses the elements of hydrogen chloride, yielding the lactonic compound  $C_6H_4{<}\begin{smallmatrix}CO\cdot CO\cdot O\\ CHCl—CCl\cdot NAcO\cdot OH\end{smallmatrix}$; rupture of the lactone ring, followed by elimination of water, and hydrolysis, leads to the substance $COOH\cdot CO\cdot C_6H_4\cdot CCl{:}CHCl$, which then passes into the indene derivative.

Orthochloronitromethoxyethylbenzoylcarboxylic acid also indifferent acetyl derivative (Abstr., 1894, i, 297); alkalis, however, do not eliminate nitrous acid from this substance, but merely regenerate the carboxylic acid. M. O. F.

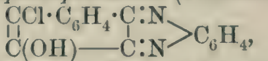
Action of Chlorine on Amido-β-naphthaquinol: Dichlorotriketohydronaphthalene, Naphthapyrogallol, and other Products of Change. By E. C. THEODOR ZINCKE and HEINRICH NOACK (*Annalen*, 1897, **295**, 7—27).—Amido-β-naphthaquinol was first obtained by Groves (Trans., 1884, **45**, 299) on reducing 3-nitro-1 : 2-dihydroxynaphthalene with tin and hydrochloric acid, the nitro-derivative being prepared by the reduction of nitro-β-naphthaquinone with stannous chloride; the hydrochloride forms silvery, lustrous leaflets, and does not change when exposed to air. The *base* crystallises in small, lustrous needles, and melts at 164°, previously darkening and decomposing; it dissolves readily in alcohol and acetone, but is very sparingly soluble in ether and benzene. The compound dissolves in alkalis and alkali carbonates, forming yellow solutions, which rapidly become brown on exposure to air, and deposit highly coloured, insoluble substances; ferric chloride gives rise to a bluish-black precipitate, and sodium nitrite converts the base or its hydrochloride into a red substance which rapidly decomposes and evolves gas. The *diacetyl* derivative separates from acetone in long, lustrous needles, and melts and decomposes at 195°; the *triacetyl* derivative crystallises from glacial acetic acid in white, lustrous needles, and decomposes above 200°.

4-*Dichloro*-1 : 2 : 3-*triketohydronaphthalene*, obtained by passing a rapid stream of chlorine into amido-β-naphthaquinol suspended in concentrated hydrochloric and glacial acetic acids, crystallises from nitric acid (sp. gr. = 1·4) in small, lustrous prisms containing $2H_2O$; it melts and decomposes at 99°, and undergoes change when boiled with alcohol. The ketone does not dissolve in sodium carbonate, which colours it red, but caustic soda forms a violet solution which yields a reddish precipitate when acidified; bleaching powder oxidises the substance to phthalic acid, phenylenediamine gives rise to an azine, and sulphuric acid converts the ketone into isonaphthazarin.

1 : 2 : 3-*Trihydroxynaphthalene* (*naphthapyrogallol*), formed from the triketochloride by reduction with stannous chloride, crystallises in lustrous prisms on adding hydrochloric acid to its solution in absolute alcohol; it becomes dark and decomposes above 250°, and rapidly decomposes when the aqueous solution is heated. The substance dissolves readily in acetone and alcohol, but with difficulty in glacial acetic acid, the solutions undergoing rapid change when heated; it dissolves in alkalis and alkali carbonates, forming almost colourless solutions which rapidly become reddish, and finally dark red. The *triacetyl* derivative crystallises from glacial acetic acid in colourless prisms or plates, and melts to a red liquid at 250—255°; nitric acid oxidises this compound to a substance which crystallises from benzene in small, reddish-yellow needles.

4-*Dichloro-3-ketonaphthaphenazine*,  $\begin{array}{l}CCl_2\cdot C_6H_4\cdot C:N \\ CO \text{———} C:N\end{array}\!\!>C_6H_4$, which is obtained on adding a solution of orthophenylenediamine in glacial acetic acid to dichlorotriketohydronaphthalene dissolved in the same medium, crystallises in beautiful, lemon yellow needles, melting and darkening at 196—197°; it dissolves with difficulty in hot alcohol and glacial acetic acid, undergoing decomposition if left for long in contact with the solvents. Concentrated sulphuric acid forms a red solution, and hot alcoholic potash develops a deep green coloration, a dark violet precipitate being formed on treatment with glacial acetic acid.

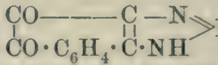
3 : 4-*Hydroxychloronaphthaphenazine* (*a-chloronaphtheurhodole*),

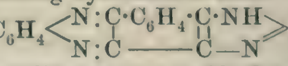


$$\begin{array}{l} CCl\cdot C_6H_4\cdot C{:}N \\ C(OH)\text{——}C{:}N \end{array}\!\!>C_6H_4,$$

prepared by reducing the foregoing naphthaphenazine in alcoholic solution with stannous chloride, crystallises from glacial acetic acid in long, lemon yellow needles melting at 199—200°; the *sodium* derivative crystallises in deep red needles, and the *hydrochloride* and *nitrate* are also red, and exhibit metallic lustre. Oxidation with nitric acid converts the eurhodole into diketonaphthaphenazine (Abstr., 1895, i, 615).

3 : 4-*Diamido*-1 : 2-*dihydroxynaphthalene* is obtained by adding diazobenzene chloride to an acidic solution of amido-β-naphthaquinol hydrochloride and reducing the azo-compound with stannous chloride; it is rapidly oxidised in air, and develops a bluish-violet coloration with sodium carbonate. The *hydrochloride* crystallises in small, lustrous needles, and dissolves very readily in water; the aqueous solution darkens on standing, but is stable in presence of free hydrochloric acid.

Azimido-β-naphthaquinone,  $\begin{array}{l} CO\text{———}C\text{—}N \\ CO\cdot C_6H_4\cdot C\cdot NH \end{array}\!\!>N$, is obtained by the action of nitrous or nitric acid on the hydrochloride of diamidodihydroxynaphthalene, and crystallises from a mixture of nitric and glacial acetic acids in small, orange-red plates, darkening above 220°; the solution in caustic soda is colourless, whilst sodium carbonate develops a brownish-red coloration. When reduced with stannous chloride, the substance yields *azimidonaphthaquinol*, which crystallises in lustrous, almost colourless, needles; the *hydrochloride* crystallises in beautiful, red needles from alcohol containing hydrochloric acid.

Azimidonaphthaphenazine,  $C_6H_4\!<\!\begin{array}{l} N{:}C\cdot C_6H_4\cdot C\cdot NH \\ N{:}C\text{———}C\text{—}N \end{array}\!\!>N$, is produced by the action of orthophenylenediamine on azimido-β-naphthaquinone, and crystallises from hot glacial acetic acid in small, bright yellow needles, undergoing no change at 250°; it is insoluble in alkalis, and forms yellow salts with acids.

M. O. F.

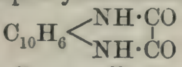
Action of Ethylic Oxalate on Aromatic Amines. III and IV.

By Richard E. Meyer and Wilhelm Müller (*Ber.*, 1897, 30, 770—774 and 775—779).—Ethylic oxalate condenses with amines of the naphthalene series, forming compounds analogous to those produced with amines of the benzene series.

With *a*-naphthylamine in the absence of alcohol, besides the ethylic *a*-naphthyloxamate already prepared by Ballo, *a dinaphthyloxamide*, $C_{10}H_7\cdot NH\cdot CO\cdot CO\cdot NH\cdot C_{10}H_7$, is produced; the latter crystallises from glacial acetic acid in slender needles melting at 234°. With β-naphthylamine, *ethylic β-naphthyloxamate*, $C_{10}H_7\cdot NH\cdot CO\cdot CO\cdot OEt$, and *β-dinaphthyloxamide* are formed, the latter crystallising from glacial acetic acid in colourless needles melting at 276°, and the former separating from boiling alcohol in colourless leaflets melting at 119·5°, *β-naphthyloxamic acid*, $C_{10}H_7\cdot NH\cdot CO\cdot COOH$, prepared from the above ethylic salt by hydrolysis with potash, forms white, glistening needles melting with effervescence at 190°. *β-Naphthyloxamide*,

$$C_{10}H_7\cdot NH\cdot CO\cdot CONH_2,$$

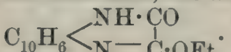
obtained by the action of ammonia on the acid, crystallises from alcohol in colourless leaflets melting at 248°.

With 1 : 2-naphthylenediamine, ethylic oxalate produces 1 : 2-*naphthylenoxamide*,  $C_{10}H_6{<}\begin{array}{l}NH\cdot CO\\ \quad\;\,|\\ NH\cdot CO\end{array}$, which crystallises from glacial acetic acid in small, yellow needles, and does not melt below 300°, whilst with 1 : 4-naphthylenediamine ethylic 1 : 4-*naphthylenedioxamate*,

$$C_{10}H_6(NH\cdot CO\cdot COOEt)_2,$$

is formed, the reaction proceeding similarly to the condensation of ethylic oxalate with paraphenylenediamine; it separates from alcohol in colourless, glistening needles melting at 203°. 1 : 4-*Naphthylenedioxamide* is an insoluble substance which does not melt at 300°; 1 : 4′-naphthylenediamine and oxalic ether, in like manner, yield *ethylic* 1 : 4′-*naphthylenedioxamate*, crystallising from alcohol in colourless needles melting at 206—208°, the corresponding *acid* melting at 235°; 1 : 4′-*naphthylenedioxamide* crystallises from boiling alcohol in slender needles and does not melt at 300°.

1 : 1′-Naphthylenediamine reacts with ethylic oxalate somewhat differently from its isomerides, the red compound of de Aguiar being produced. For this substance, the authors propose the formula



$$C_{10}H_6{<}\begin{array}{l}NH\cdot CO\\ \quad\;\;\;\,|\\ N{=}C\cdot OEt\end{array}.$$

J. F. T.

Constitution of Cymene and of the Terpene in Cummin Oil (Cuminum cyminum). By L. J. Wolpian (*Chem. Centr.*, 1896, i, 920—921, 1067; from *Pharm. Zeit. Russ.*, **35**, 97—101, 145—149).—The oil of cummin used by the author had a specific gravity = 0·892 at 18°, and a rotatory power of + 7° 23′ in a 100 mm. tube. The portion distilling below 220° was treated with sodium hydrogen sulphite solution and fused potassium hydroxide, then boiled with metallic sodium and again distilled. The clear, strongly refractive liquid thus obtained had the odour of eucalyptus oil, and consisted of cymene and terpene, which cannot, however, be completely separated by fractionation. The fraction distilling at 160—169° showed a rotation of about + 20°, that at 169—176° of about + 8°. From the latter, which is rich in cymene, the terpene (pinene?) was isolated by conversion into the hydrochloride, which boils at 208°, by passing in dry hydrogen chloride at − 18°, then shaking the saturated solution with water and sodium carbonate solution, drying, and finally fractionating under 40 mm. pressure with a Löbel's dephlegmator. The largest fraction, boiling at 103—106°, showed a rotation of + 1° 17′ and was again submitted to the same treatment. In this way, pure cymene boiling at 173·5—174·5° under 763 mm. pressure, of sp. gr. = 0·8588 at 20° and 0·8595 at 15° and of refractive index 1·479, was obtained. It was further identified as methylisopropylbenzene by conversion into the barium salts of α- and β-sulphocumic acids (Klaus), by preparation of the sodium salt of α-sulphocumic acid (from the α-barium salt) and of the α-sulphonamide melting at 115—116°. The α-sulphonamide of normal methylpropylbenzene melts at 101—102°.

From a comparison with cymene from cummin, the author regards all cymenes found in ethereal oils and obtained from terpenes as being the isopropyl compound. Attempts to convert cymene into terpene gave unsatisfactory results. The portions distilling below 170° obtained from the purified mixture of cymene and terpene, after repeated fractionation over sodium, gave a terpene of boiling point 157—158° at 768 mm. pressure, of sp. gr. = 0·8604 at 20°, and specific rotatory power $[\alpha]_D = +29·46$. By passing hydrogen chloride into a solution of this terpene in carbon bisulphide, an optically inactive liquid hydrochloride was obtained, of which the greater portion boils at 142—158° under 50 mm. pressure, and has a sp. gr. = 0·94 at 16°. A liquid bromide, $C_{10}H_{16}Br_2$, easily soluble in alcohol, ether, and chloroform, of sp. gr. = 1·1243 at 18°, and specific rotatory power $[\alpha]_D = +7·04$ was prepared by bromination in acetic acid solution. The author was unable to obtain a crystalline nitrosyl chloride compound of hydrocumene by Wallach's method, and believes that this incapacity of the terpene of oil of cummin to form crystalline compounds shows it to be different from the terpenes hitherto examined. This terpene is very similar to Flawitzky's terpene prepared from Russian turpentine oil.

E. W. W.

The Chemical and Industrial Importance of Ethereal Oils. Cinnamon Oils. By DUYK (*Chem. Centr.*, 1896, ii, 358; from *J. Pharm. d'Anvers*, 1896, April).—Whilst the German, American, and Swiss pharmacopœias prescribe the oil of *Cinnamomum cassia*, in Belgium the oil from the bark of *C. zeylanica* is officinal. The latter has a density of 1·024, contains about 60 per cent. of cinnamaldehyde, and is optically inactive. Its alcoholic solution is said to give with ferric chloride a pale green, and not the bluish-green coloration indicative of eugenol. The oil contains 6—8 per cent. of eugenol, phellandrene, and small quantities of safrole, &c., whilst that from the leaves and roots of the same plant consists chiefly of eugenol and a solid "camphor." The Ceylon cinnamon oil is much adulterated. The inferior Cassia oil of density 1·055—1·065 contains 70—78 per cent. of cinnamaldehyde besides cinnamylic acetate, eugenol, a terpene, and methylorthocumaraldehyde. It is miscible with strong alcohol, and its alcoholic solution turns brown with ferric chloride. It is often adulterated with paraffin or colophony. A good oil, on distillation, should not leave a residue of more than 8—10 per cent.

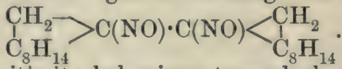
E. W. W.

Action of Hydrogen Chloride on Licareol, Licarhodol, and Lemonol. By PHILIPPE BARBIER and LOUIS BOUVEAULT (*Bull. Soc. Chim.*, 1896, [iii], 15, 594—597. Compare Abstr., 1893, i, 514).—When hydrogen chloride is passed into lemonol, obtained from the oil of

Andropogon Schœnanthus, it is readily absorbed, an oily product boiling at 120—125° (10 mm.), and having a sp. gr. = 1·0569 being obtained. The composition of this oil, which contains a little unaltered lemonol, is represented by the formula $C_{10}H_{18}Cl_2$. When heated with an acetic acid solution of fused potassium acetate and distilled, it yields two fractions, the first boiling at 170—180°, and consisting of a mixture of quadrivalent terpenes, whilst the second consists of the acetate of lemonol, $C_{10}H_{17}OAc$. The latter, on hydrolysis, gives pure inactive lemonol boiling at 114—116° (10 mm.). This reaction points to the existence in the oily hydrochloride of two isomeric substances, the one saturated, the other unsaturated ; the former yielding the mixture of terpenes, the latter the acetate. The amount of bromine with which this oil is capable of uniting points to the existence in it of these two substances in nearly equal proportions. Licareol, saturated with hydrogen chloride, yields a product which can be easily converted into acetate of lemonol, and then into lemonol itself. Licarhodol, produced by isomeric change from licareol when the latter is heated with acetic anhydride, yields, on saturation with hydrogen chloride, the same mixture of hydrochlorides. The author insists that licareol and licarhodol are two distinct alcohols, rotating the plane of polarised light in opposite senses, but easily converted into the optically inactive alcohol, lemonol. A. C. C.

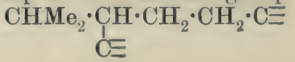
Researches on Camphor. By Enrico Rimini (*Gazzetta*, 1896, **26**, ii, 502—517).—An almost quantitative yield of fenchonoxime is obtained by cautiously heating a solution of pure fenchone (70 grams) in alcohol (300 c.c.) with hydroxylamine hydrochloride (50 grams) and stick soda (140 grams) on the water bath, and, after several hours' boiling, adding a similar quantity of hydroxylamine salt in two portions ; the alcohol is partially distilled off, the residual solution precipitated by water, and the oxime recrystallised from light petroleum. Fenchonoxime melts at 165°, and is nearly insoluble in alkali. When its dilute hydrochloric acid solution is treated with sodium nitrite, a violent reaction occurs, and *pernitrosofenchone*, $C_{10}H_{16}N_2O_2$, is formed ; it crystallises in transparent, white scales melting at 66—67°, and has an odour resembling that of the isomeric pernitrosocamphor. Like the latter, it probably contains the group $:CN_2O_2$. When heated with alcoholic potash, it yields fenchone, but if treated with cold alcoholic potash or ammonia it is converted into the isomeric *isopernitrosofenchone*, which crystallises in colourless, orthorhombic tablets [$a : b : c = 0·6775 : 1 : 0·4626$] melting at 88° ; the reverse change could not be effected. Pernitrosofenchone is converted into fenchone by boiling with hydroxylamine hydrochloride in alkaline solution and into isocamphor (Angeli & Rimini, this vol., i, 88) by concentrated sulphuric acid ; isocamphor is also obtained by treating isopernitrosofenchone with concentrated sulphuric acid.

Pernitrosomenthone, $C_{10}H_{18}N_2O_2$, is prepared by the action of sodium nitrite on menthonoxime dissolved in acetic acid ; it is an oil which, when distilled under reduced pressure decomposes at 140°, and is converted into menthone by treatment with sulphuric acid or alkalis. Menthonoxime yields menthone when oxidised by alkaline potassium ferricyanide solution.

Camphoroxime is oxidised by potassium ferricyanide in cold soda solution, yielding a bright blue compound $(C_{10}H_{15}NO)_2$, which melts at 104—105°, and gives a blue solution in light petroleum; it has the normal molecular weight in freezing benzene, and probably has the constitution  $\begin{matrix}CH_2\\|\\C_8H_{14}\end{matrix}>C(NO)\cdot C(NO)<\begin{matrix}CH_2\\|\\C_8H_{14}\end{matrix}$. This constitution is in accordance with its behaviour towards hydrochloric acid, which converts it into a mixture of camphoroxime and camphor. W. J. P.

Action of Nitrous Acid on Camphoroxime. By ANGELO ANGELI and ENRICO RIMINI. (*Gazzetta*, 1896, **26**, ii, 517—521).—The acid of the composition $C_8H_{14}O_4$, previously prepared by the authors (this vol., i, 89) by oxidising isocamphor, easily forms an anhydride, and yields succinic acid when oxidised with chromic acid; it may be synthesised by reducing diethylic isoproplyacetonedicarboxylate, and is identical with an α-isopropylglutaric acid prepared by W. H. Perkin, jun. (Trans., 1896, 1495). The identity of the authors' preparation with that of Perkin is established by a crystallographic examination of the anilides; they are orthorhombic [$a : b : c = 0{\cdot}9520 : 1 : 2{\cdot}7383$] and melt at about 160°.

It follows that isocamphor contains the group



$$CHMe_2\cdot\underset{\underset{C\equiv}{|}}{CH}\cdot CH_2\cdot CH_2\cdot C\equiv$$

W. J. P.

Asafœtida. By J. POLÁSEK (*Arch. Pharm.*, 1897, **235**, 125—132).—Pure drops of *Asafœtida amygdaloides* gave the following results on analysis:—Resin soluble in ether = asaresinotannol ferulate, 61·40; resin insoluble in ether = free asaresinotannol, 0·60; gum, 25·1; ethereal oil, 6·7; vanillin, 0·06; ferulic acid, 1·28; moisture, 2·36 per cent. On hydrolysis with potassium carbonate, the soluble resin yields a resinotannol, named asaresinotannol by the author, and ferulic acid; on hydrolysis with sulphuric acid, however, it is decomposed into the same tannol and umbelliferone. The author has succeeded in obtaining umbelliferone by the action of sulphuric acid (55 per cent.) on a mixture of ferulic acid and resorcinol; guaiacol is formed at the same time. *Asaresinotannol*, $C_{24}H_{34}O_5$, is a brownish-yellow powder, readily soluble in alcohol, potash, acetone, chloroform, amylic alcohol, and acetic acid, sparingly so in ether, benzene, carbon bisulphide or ammonia, but insoluble in light petroleum. Since it yields a *monobenzoyl* and a *monacetyl* derivative, it contains a hydroxyl group. On oxidation with nitric acid, it yields picric acid. J. J. S.

Glucosides of Black and White Mustards. By J. GADAMER (*Arch. Pharm.*, 1897, **235**, 44—114. Compare this vol., i, 254).—The silver compound, $C_4H_5NAg_2S_2O_4 + H_2O$, obtained by the action of silver nitrate on an aqueous solution of sinigrin, is formed according to the equation $C_{10}H_{16}KNS_2O_9 + 2AgNO_3 + H_2O = C_4H_5NAg_2S_2O_4 + C_6H_{12}O_6 + KNO_3 + HNO_3$; this was proved by estimating the acidity and rotatory power of the resulting liquid. The silver compound is undoubtedly not a simple molecular compound of phenylthiocarbimide with normal silver sulphate, as it cannot be obtained by mixing these two compounds. Its behaviour with ammonia also speaks against this additive constitution.

Hydrochloric acid decomposes the compound, yielding silver chloride, free sulphur, sulphuric acid, and probably allylic cyanide; it is also decomposed when heated alone or with water, the products being phenylthiocarbimide, silver sulphide and sulphate, and carbon bisulphide. All these reactions indicate that the two atoms of silver are differently situated in the molecule. A similar *mercury* compound can be obtained by treating a solution of sinigrin with mercurous nitrate, or by the action of metallic mercury on the silver salt. When solutions of sinigrin and silver nitrate in the proportion of 3 mols. of the former to 4 of the latter are mixed, no precipitate is obtained, owing to the formation of a double compound, $C_4H_5SNAg_2SO_4 + C_4H_5SNAgKSO_4$.

A solution of sinigrin when added to barium chloride, yields no precipitate of barium sulphate in the cold, but complete decomposition ensues when the mixture is heated; barium hydroxide, on the other hand, yields a precipitate at once; in this respect, sinigrin resembles potassium ethylsulphate. The author has studied the action of ammonia on sinigrin both under pressure and in the cold, but no definite products could be isolated. An acetic acid solution of phenylhydrazine decomposes sinigrin and yields phenylglucosazone (m. p. 204°).

Sinalbin (compare Will and Laubenheimer, *Annalen*, **199**, 150, and this vol., i, 255) occurs in white mustard, but no trace of it can be found in black, and similarly no trace of sinigrin is to be found in white mustard. Sinalbin reacts with barium chloride or hydroxide in exactly the same manner as sinigrin.

Sinapin iodide, when anhydrous, melts at 178—179°, and forms a periodide when heated with alcoholic iodine solution at 100°. The crystalline bromide, $C_{16}H_{24}NO_5Br + 3H_2O$, melts at 90—92°, but the anhydrous salt at 107—115°. *Sinapin nitrate*, $C_{16}H_{24}NO_5 \cdot NO_3$, is readily soluble in water, but crystallises from alcohol with $2H_2O$.

Ethylic sinapate, $C_{11}H_{11}O_5Et + H_2O$, crystallises in colourless scales, melts at 80—81°, and is insoluble in water but readily dissolves in ether and alcohol; it loses its water of crystallisation when kept over sulphuric acid, and becomes soft. *Acetylsinapic acid* crystallises in needles and melts at 181—187° and not at 281° as stated by Remsen and Coale (Abstr., 1884, 1388); the author has proved that it is a monacetyl derivative by estimating the amount of acetic acid formed on hydrolysis. When heated with hydriodic acid, sinapic acid yields methylic iodide, the amount formed corresponding with two methoxy-groups in the original acid. *Methylic methylsinapate*, which crystallises in yellowish plates and melts at 91—91·5°, when hydrolysed, yields *methylsinapic acid*, melting at 123·5—124°. This acid, when oxidised with an alkaline solution of potassium permanganate, yields trimethylgallic acid, $C_6H_2(OMe)_3COOH$ [$COOH : (OMe)_3 = 1 : 3 : 4 : 5$.] No definite oxidation product could be obtained from sinapic acid.

J. J. S.

Constituents of the Root of Ononis Spinosa, L. By HERMANN THOMS (*Arch. Pharm.*, 1897, **235**, 28—39).—Ononin, a constituent of the root of *Ononis spinosa*, is usually contaminated with more or less of a wax-like substance, which Hlasiwetz (*J. pr. Chem.*, 1855, **65**, 419) termed onocerin. The author has prepared larger quantities of the latter by extracting the root with 90 per cent. alcohol and then treating the extract with 60 per cent. alcohol in which onocerin is insoluble. It crystallises in minute prisms, melts at 232°, and is but sparingly soluble in the usual organic solvents; it dissolves more readily, however, in amylic alcohol, turpentine, or glacial acetic acid. If dissolved in concentrated sulphuric acid, it gives a yellow solution, and when sulphuric acid is poured into an acetic acid solution, a bluish-green band is formed at the junction of the two liquids, the acetic acid solution becoming red after a time. Onocerin has the composition $C_{26}H_{44}O_2$; it yields a *diacetyl* derivative melting at 224°, and probably a *dibenzoyl* derivative. Bromine reacts with an acetic acid solution of the acetyl compound, yielding a *tetrabromide*, $C_{26}H_{42}O_2Ac_2,Br_4$ or $C_{26}H_{38}Br_4O_2Ac_2$. When oxidised with chromic mixture, onocerin is converted into a diketone, *onoketone*, $C_{26}H_{40}O_2$, which melts at 186—187°. The *hydrazone*, $C_{26}H_{40}(N{\cdot}NHPh)_2$, *ketoxime*; $C_{26}H_{40}(NOH)_2$, and *semicarbazone*, $C_{26}H_{40}ON{\cdot}NH{\cdot}CO{\cdot}NH_2$, are described. Onoketone, when further oxidised with chromic mixture, yields acetic and butyric acids, together with an *acid*, $C_{20}H_{38}O_2$, which melts at 73—74°, and a resinous *acid*, $C_{20}H_{35}O_5$. It is probable that other products are also formed.

The author suggests the name *onocol* instead of onocerin for the original compound, since it is undoubtedly a secondary alcohol. J. J. S.

Phytosterin. By Hermann Thoms (*Arch. Pharm.*, 1897, **235**, 39—43).—The term phytosterin was first introduced by Hesse (*Annalen*, 1878, **192**, 175) for vegetable cholesterol. Other investigators have shown that, not only is vegetable cholesterol different from animal cholesterol, but also that the former differs in certain of its physical properties according to the source from which it is obtained. The author points out that other substances of vegetable origin, for example, cynanchol (*Annalen*, 1878, **192**, 152), quebrachol (*ibid.*, 1882, **211**, 272), cupreol (*ibid.*, 1885, **228**, 288, and 1886, **234**, 375), cinchol, lactucerol (*ibid.*, **234**, 243), urson (*Monatsheft.*, 1893, **14**, 255), amyrin (*Ber.*, 1887, **20**, 1242, and 1891, **24**, 3836), and lupeol (*ibid.*, 1891, **24**, 2709), give not only Liebermann's colour reaction (*Ber.*, 1885, **18**, 1804), but also Hesse's reaction for cholesterol. Other substances, such as onocol, onoketone (see preceding abstract), benzoresinol (*Arch. Pharm.*, 1893, **233**, 209), and abietic acid also give the same reactions. It is obvious that these characteristic cholesterol reactions do not simply depend on the alcoholic character of the substances, since certain resinous acids also give them. The author suggests that the term phytosterin should be given to all unsaturated alcohols of high molecular weight which give the characteristic cholesterol colour reactions, and which owe their origin to physiological processes similar to those which produce cholesterol. J. J. S.

Compounds from Lichens. By Wilhelm Zopf (*Annalen*, 1897, **295**, 222–256. Compare this vol., i, 255).—The sources and properties of atranoric acid, $C_{19}H_{18}O_8$, and hæmatommic acid, $C_{11}H_{12}O_5$, obtained from it by the action of absolute alcohol at 150°, have been already indicated (*loc. cit.*). *Atranorinic acid* is produced when atranoric acid is heated with water in sealed tubes at 150°, and crystallises in colourless needles; it melts at about 101°, dissolves somewhat readily in hot water, and forms a yellow solution in alkalis. *Atraric acid* is also obtained from atranoric acid by the action of water, and crystallises in thin, micaceous leaflets; it melts at about 140—141°, dissolves sparingly in hot water, and does not form yellow solutions with alkalis.

Psoromic acid (compare Abstr., 1895, i, 298) crystallises in small, snow-white needles, and melts to a dark brown liquid at 263–265°; it dissolves freely in acetone, but only very sparingly in cold ether, chloroform, and alcohol, these solvents dissolving it more readily when heated. It is scarcely soluble in benzene, and cold alkali carbonates dissolve it with difficulty, whilst caustic alkalis form yellow or reddish-yellow solutions; a dilute alcoholic solution develops a deep red coloration with ferric chloride. The alkali salts are very characteristic, crystallising in rosettes of dark red needles, and being readily soluble in water, must be precipitated from solution by treatment with carbonic anhydride; the barium and calcium salts are reddish-brown and do not dissolve in water.

Usnic acid (compare Abstr., 1895, i, 298; 1896, i, 104; also this vol., i, 256) crystallises in yellowish-green prisms, melts at 195—197°, and decomposes above 200°, yielding a carbonaceous residue; it is very sparingly soluble in hot alcohol, ether, and light petroleum, but dissolves freely in hot chloroform and benzene. It dissolves with difficulty in aqueous ammonia, more readily in caustic alkalis and solutions of the alkaline earths, with development of a yellow coloration, which becomes brown on heating the liquid; ferric chloride develops a brownish-red coloration with an alcoholic solution of the substance. Usnic acid is most conveniently identified by converting it into decarbusnein, which is obtained by heating the acid with absolute alcohol in sealed tubes at 150°; this crystallises from dilute alcohol in slender, colourless needles, and melts at 175°.

Stereocaulic acid (Abstr., 1896, i, 104) is obtained in quantity amounting to about 0·7 per cent. from *Stereocaulon alpinum*, collected on the Col di Rodella, in the Dolomites; it crystallises from alcohol in hemispherical aggregates of minute, lustrous prisms, has the empirical formula $C_9H_{10}O_3$, and melts at 193—195° (compare *loc. cit.*). The alcoholic solution reddens litmus, and develops a beautiful violet coloration with ferric chloride; the substance is insoluble in light petroleum, dissolves with great difficulty in cold alcohol, ether, benzene, and chloroform, freely, however, in boiling alcohol and glacial acetic acid. The *acetyl* derivative is obtained by the action of acetic anhydride, and crystallises from absolute alcohol in aggregates of minute needles melting at 186—187°; hydrolysis with dilute potash regenerates stereocaulic acid, along with a certain amount of orcin.

Salazinic acid, extracted by chloroform from *Stereocaulon salazinum* (Bory), is a microcrystalline powder which darkens at 235° and becomes blackish-brown at 250° without undergoing fusion; it dissolves in hot alcohol, ether, chloroform, and glacial acetic acid with difficulty, and is insoluble in boiling benzene. Alkali carbonates yield yellow solutions which darken when heated, and after some time deposit the alkali salts in minute, red needles which resemble the salts of psoromic acid. *Stereocaulon denudatum* (Flörke), *var. pulvinatum* (Schaerer), which is identical with *var. compactum* (Körber), contains atranoric and psoromic acids.

Catocarpus alpicolus (Wahlbg.), or *Catocarpon chionophilum* (Fries) closely resembles *Rhizocarpon geographicum* morphologically, and has been classified by Körber as *var. alpicolum* of that group; it is now found that the resemblance extends to the composition of the lichens, which both contain psoromic and rhizocarpic acids. The latter substance is also present in *Biatora lucida* (compare Abstr., 1895, i, 298), which does not, as stated by Knop, contain usnic acid; *Rhizocarpon geographicum* is also destitute of usnic acid.

An analogous chemical resemblance has been traced between *Candelaria concolor* (Dickson), which is identical with *Xanthoria concolor* (Fries), *Candelaria vulgaris* (Massalongo), and *Lecanora laciniosa* (Duf. and Nylander), and the two closely allied lichens, *Callopisma vitellinum* (Ehrhardt) and *Physcia medians* (Nylander); all three contain calycin and callopismic (ethylpulvic) acid.

It has been shown (Abstr., 1896, i, 103) that *Physcia cæsia* (Hoffmann) or *Parmelia cæsia* (Acharius), when collected in sandy districts, contains atranoric and hæmatommic acids, along with zeorin; this is also the case when the lichen is dolomitic. *Placodium crassum* (Hudson), from this source, also resembles that obtained from North Germany, both specimens being destitute of psoromic acid, and giving indications of the presence of usnic acid; Spica, however (Abstr., 1883, 80), states that both acids are present in Sicilian *Placodium*. *Placodium Lagascæ* (Ach.), a rare chalk lichen occurring in the Dolomites, contains psoromic and usnic acids, along with a substance which has not been further investigated; it is destitute of atranoric acid, hæmatommic acid, and zeorin.

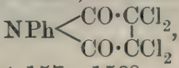
An instance of two varieties, or morphologically allied forms, differing from one another chemically, is afforded by *Placodium melanaspis, var. stellata* (Fries), and *P. m. var. alphoplaca* (Wahlenberg); as already stated (*loc. cit.*), the former contains atranoric acid and placodin, but it is now found that the *var. alphoplaca* contains psoromic acid along with a compound which, although red, is not identical with placodin.

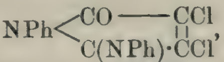
Hæmatomma ventosum (Laurer, Schaerer) contains usnic acid and *ventosaric acid*, which crystallises in colourless prisms and melts at 205—207°; caustic soda develops a yellow coloration, which gradually becomes purple, and finally violet.

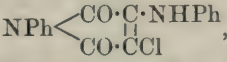
Lecanora thiodes (Sprengel) contains atranoric acid and zeorin.

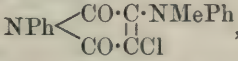
M. O. F.

Action of Phosphorus Pentachloride on Imides of Dibasic Acids. By Richard Anschütz (*Annalen*, 1897, **295**, 27—28).—Introductory to the following abstracts. M. O. F.

Action of Phosphorus Pentachloride on Succinanil and Dichloromaleinanil. By Richard Anschütz and Charles Beavis (*Annalen*, 1897, **295**, 29—43. Compare Abstr., 1895, i, 176).—It has been shown that phosphorus pentachloride converts succinanil into tetrachloro-1-phenylpyrolline and dichloromaleinanil dichloride (*loc. cit.*); the latter substance is also formed when the chloride acts on dichloromaleinanil, the main product, however, consisting of *tetrachlorosuccinanil*,  $\mathrm{NPh}<\begin{array}{l}\mathrm{CO\cdot CCl_2}\\ \quad\;|\\ \mathrm{CO\cdot CCl_2}\end{array}$, which crystallises from methylic alcohol and melts at 157—158°.

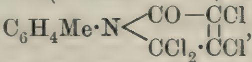
Dichloromaleindianil,  $\mathrm{NPh}<\begin{array}{l}\mathrm{CO}\;\text{——}\;\mathrm{CCl}\\ \qquad\qquad\;\|\\ \mathrm{C(NPh)\cdot CCl}\end{array}$, is obtained by adding aniline dissolved in chloroform to dichloromaleinanil dichloride in the same medium, and crystallises from acetone in yellow cubes melting at 186—187°.

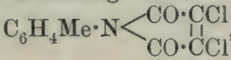
Anilidochloromaleinanil,  $\mathrm{NPh}<\begin{array}{l}\mathrm{CO\cdot C\cdot NHPh}\\ \qquad\|\\ \mathrm{CO\cdot CCl}\end{array}$, is produced on heating dichloromaleinanil with aniline and a small quantity of chloroform in closed tubes at 100°; it crystallises from alcohol or acetone in yellow, prismatic needles, and melts at 188—189°.

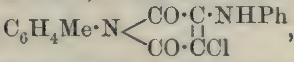
Methylanilidochloromaleinanil,  $\mathrm{NPh}<\begin{array}{l}\mathrm{CO\cdot C\cdot NMePh}\\ \qquad\|\\ \mathrm{CO\cdot CCl}\end{array}$, is obtained by heating dichloromaleinanil dichloride with methylaniline and chloroform in sealed tubes at 100°, and separates from acetone in small, yellowish-brown crystals melting at 188—189°; it is also formed when dichloromaleinanil and methylaniline are heated in chloroform at 100°.

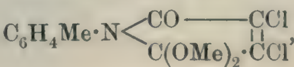
Reduction of dichloromaleinanil dichloride with sodium amalgam leads to the formation of γ-anilidobutyrolactam (*loc. cit.*), and when this is hydrolysed and treated with silver nitrate, *silver* γ-anilidobutyrate is obtained; the *hydrochloride* of γ-anilidobutyric acid melts at 135·5—136·5°. M. O. F.

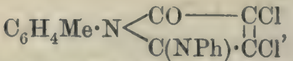
Action of Phosphorus Pentachloride on Succinoparatolil.

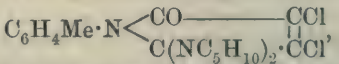
By Richard Anschütz and Alfred Guenther (*Annalen*, 1897, **295**, 43—55).—*Dichloromaleinparatolil dichloride*,  $\mathrm{C_6H_4Me\cdot N}<\begin{array}{l}\mathrm{CO-CCl}\\ \qquad\;\|\\ \mathrm{CCl_2\cdot CCl}\end{array}$, is obtained by heating succinoparatolil with phosphorus pentachloride in a reflux apparatus at 80° and subsequently at 120°, and after crystallisation from benzene, melts at 156°; the crystals belong to the monosymmetric system; $a:b:c = 0·4422:1:0·4680$, and $\beta = 83° 3'$. The *compound*, $C_{11}H_{10}Cl_4NPO_2$, occurs as a bye-product, and separates from hot acetone in white crystals melting at 237°.

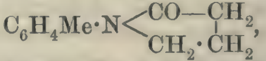
Dichloromaleinparatolil,  $\mathrm{C_6H_4Me\cdot N}<\begin{array}{l}\mathrm{CO\cdot CCl}\\ \qquad\|\\ \mathrm{CO\cdot CCl}\end{array}$, is obtained by treating the dichloride with boiling water, or boiling dilute alcohol; it crystallises from alcohol in long, silky needles, and melts at 193°.

Anilidochloromaleinparatolil,  $\mathrm{C_6H_4Me\cdot N}<\begin{array}{l}\mathrm{CO\cdot C\cdot NHPh}\\ \qquad\|\\ \mathrm{CO\cdot CCl}\end{array}$, is produced when dichloromaleinparatolil is heated with aniline and chloroform in a sealed tube, and crystallises from acetone in yellow scales melting at 40°; *piperidochloromaleinparatolil* crystallises from acetone in yellow scales, and melts at 130°.

Dichloromaleinparatolil dimethyl ether,  $\mathrm{C_6H_4Me\cdot N}<\begin{array}{l}\mathrm{CO}\;\text{——}\;\mathrm{CCl}\\ \qquad\qquad\;\|\\ \mathrm{C(OMe)_2\cdot CCl}\end{array}$, is formed on adding dichloromaleintolil dichloride to hot, absolute methylic alcohol, and melts at 98°; the *diethyl ether*, which melts at 88°, belongs to the monosymmetric system; $a:b:c = 0{\cdot}3888:1:0{\cdot}3945$; $\beta = 78° 9'$.

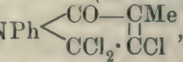
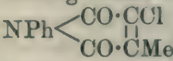
Dichloromaleinparatolilanil,  $C_6H_4Me\cdot N<\begin{array}{l}CO\text{——}CCl\\ C(NPh)\cdot CCl\end{array}$, is obtained on allowing a mixture of dichloromaleintolil dichloride and aniline dissolved in chloroform to stand for some days; it crystallises from alcohol or acetone in scales or prismatic needles, and melts at 141°; *dichloromaleindiparatolil* crystallises from acetone in yellow needles, and melts at 161°.

Dichloromaleinparatolildipiperidide,  $C_6H_4Me\cdot N<\begin{array}{l}CO\text{————}CCl\\ C(NC_5H_{10})_2\cdot CCl\end{array}$, is obtained by heating dichloromaleintolil dichloride with piperidine and benzene in sealed tubes at 100° for 24 hours; it separates from acetone in bright yellow, transparent crystals, and melts at 107°. The crystals are monosymmetric; $a:b:c = 0{\cdot}9869:0{\cdot}7464$; $\beta = 63° 44'$.

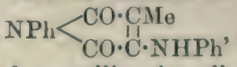
γ-Paratoluididobutyrolactam,  $C_6H_4Me\cdot N<\begin{array}{l}CO\text{—}CH_2\\ CH_2\cdot CH_2\end{array}$, is obtained from dichloromaleinparatolil dichloride by reducing it with sodium amalgam; it crystallises from water in small needles melting at 82°, and boils at 189° under a pressure of 13 mm. Hydrolysis with barium hydroxide gives rise to *barium* γ-paratoluididobutyrate; the *silver* salt is sparingly soluble.

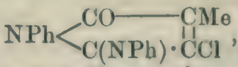
M. O. F.

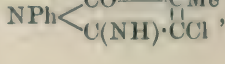
Action of Phosphorus Pentachloride on Citraconanil. By Richard Anschütz and Julius Meyerfeld

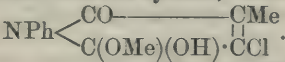
(*Annalen*, 1897, **295**, 56—66).—*Chlorocitraconanildichloride,*  $NPh<\begin{array}{l}CO\text{—}CMe\\ CCl_2\cdot CCl\end{array}$, prepared from citraconanil by the action of phosphorus pentachloride, crystallises from ether in white prisms melting at 103°. Boiling water or dilute alcohol converts it into *chlorocitraconanil,*  $NPh<\begin{array}{l}CO\cdot CCl\\ CO\cdot CMe\end{array}$, which crystallises from alcohol in needles melting at 135°, and boils at 190° under a pressure of 19 mm. *Chlorocitraconanilic acid,*

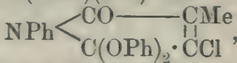
$COOH\cdot CMe{:}CCl\cdot CO\cdot NHPh$, or $COOH\cdot CCl{:}CMe\cdot CO\cdot NHPh$,

is formed on hydrolysing citraconanil with barium hydroxide, and also by the action of aniline on an ethereal solution of chlorocitraconic anhydride. *Anilidocitraconanil,*  $NPh<\begin{array}{l}CO\cdot CMe\\ CO\cdot C\cdot NHPh\end{array}$, is obtained from chlorocitraconanil and aniline, and crystallises in yellow plates melting at 157°.

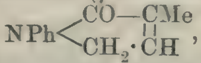
Chlorocitracondianil,  $NPh<\begin{array}{l}CO\text{——}CMe\\ C(NPh)\cdot CCl\end{array}$, is prepared from chlorocitraconanil dichloride and aniline, and crystallises from alcohol in slender, yellowish plates melting at 125°; further treatment with aniline at 120° yields anilidocitraconanil, and not the dianil.

Chlorocitraconimidoanil,  $NPh<\begin{array}{l}CO\text{——}CMe\\ C(NH)\cdot CCl\end{array}$, is obtained by adding alcoholic ammonia to an ethereal solution of chlorocitraconanil dichloride, and crystallises from ether in golden yellow needles melting at 116°.

When methylic alcohol acts on chlorocitraconanil dichloride, the *compound* $C_{12}H_{12}NO_3Cl$ is produced; it separates from light petroleum in crystals belonging to the triclinic system, melts at 114°, and probably has the constitution  $\mathrm{NPh}<\begin{array}{l}\mathrm{CO}\text{————}\mathrm{CMe}\\ \mathrm{C(OMe)(OH)\cdot \overset{\|}{C}Cl}\end{array}$.

Chlorocitraconanil diphenyl ether,  $\mathrm{NPh}<\begin{array}{l}\mathrm{CO}\text{———}\mathrm{CMe}\\ \mathrm{C(OPh)_2\cdot \overset{\|}{C}Cl}\end{array}$, obtained by boiling a solution of chlorocitraconanil dichloride in benzene with phenol, separates from light petroleum in aggregates of scales melting at 125°.

a-Methyl-γ-anilidocrotonolactam (γ-anilidotiglolactam),

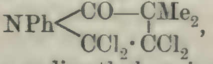


$$\mathrm{NPh}<\begin{array}{l}\mathrm{CO{-}CMe}\\ \mathrm{CH_2\cdot \overset{\|}{C}H}\end{array},$$

is prepared by reducing chlorocitraconanil dichloride in ethereal solution with sodium amalgam; it crystallises in beautiful, long needles or prisms, and melts at 97—97·5°. Hydrolysis with barium hydroxide gives rise to α-methyl-γ-anilidocrotonic acid. M. O. F.

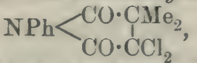
Action of Phosphorus Pentachloride on Asymmetric Dimethylsuccinanil, Dichloromaleinimide, and Succinimide. By Richard Anschütz and Georg Schroeter (*Annalen*, 1897, **295**, 67—93).

—*Asymmetric dimethyldichlorosuccinanil dichloride*,

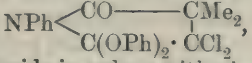
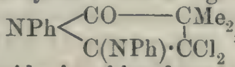


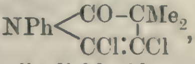
$$\mathrm{NPh}<\begin{array}{l}\mathrm{CO{-}CMe_2}\\ \mathrm{CCl_2\cdot \overset{|}{C}Cl_2}\end{array},$$

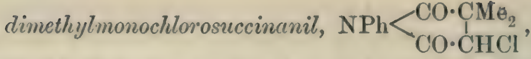
is prepared by submitting *as*-dimethylsuccinanil to the action of phosphorus pentachloride at 60—70°; it crystallises from light petroleum in rhombic plates and melts at 86·5—87°, boiling at 191—192° under a pressure of 9 mm. *Asymmetric dimethyldichlorosuccinanil*,

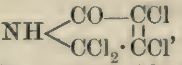
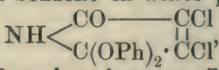


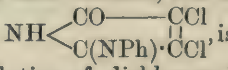
$$\mathrm{NPh}<\begin{array}{l}\mathrm{CO\cdot CMe_2}\\ \mathrm{CO\cdot \overset{|}{C}Cl_2}\end{array},$$

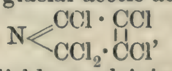
is obtained from the dichloride by the action of water, and crystallises in needles melting at 114°; it boils at 179—180·2° under a pressure of 10·5 mm. The *diphenyl ether*,  $\mathrm{NPh}<\begin{array}{l}\mathrm{CO}\text{———}\mathrm{CMe_2}\\ \mathrm{C(OPh)_2\cdot \overset{|}{C}Cl_2}\end{array}$, is produced on heating a solution of the dichloride in xylene with phenol at 120—125°; it separates from benzene in lustrous crystals containing the solvent, and melts at 156—157°. The *dianil*,  $\mathrm{NPh}<\begin{array}{l}\mathrm{CO}\text{———}\mathrm{CMe_2}\\ \mathrm{C(NPh)\cdot \overset{|}{C}Cl_2}\end{array}$, arises from the action of aniline on the dichloride in chloroform solution; it crystallises from acetone in rosettes of prisms, and melts at 129°.

a-Dimethyl-βγ-dichloro-γ-anilidoisocrotonolactam,  $\mathrm{NPh}<\begin{array}{l}\mathrm{CO{-}CMe_2}\\ \mathrm{CCl{:}\overset{|}{C}Cl}\end{array}$, is obtained on reducing *as*-dimethyldichlorosuccinanil dichloride with sodium amalgam, and when crystallised from xylene melts at 99°; it is also produced when the dichloride is heated with mercury diphenyl and benzene at 170—180°. The dichloride is regenerated when the product is heated with phosphorus pentachloride.

Asymmetric dimethylmonochlorosuccinanil,  $NPh<\begin{matrix}CO\cdot CMe_2\\ CO\cdot CHCl\end{matrix}$, is produced on exposing the foregoing lactam to moist air, or by heating it with glacial acetic acid; it crystallises in small, lustrous needles, and melts at 163°.

Dichloromaleinimide chloride,  $NH<\begin{matrix}CO—CCl\\ CCl_2\cdot CCl\end{matrix}$, is prepared by heating dichloromaleinimide with phosphorus pentachloride in sealed tubes for 2—3 hours at 160°; it crystallises from benzene in white prisms, and melts at 147—148°; the *diphenyl ether*,  $NH<\begin{matrix}CO——CCl\\ C(OPh)_2\cdot CCl\end{matrix}$, is obtained by heating the dichloride with phenol and xylene at 70—80°; it crystallises from benzene in small needles, and melts at 170°.

Dichloromaleinimideanil,  $NH<\begin{matrix}CO——CCl\\ C(NPh)\cdot CCl\end{matrix}$, is produced by the action of aniline on an ethereal solution of dichloromaleinimide chloride, and when crystallised from glacial acetic acid melts at 151—152°.

Pentachloropyrroline,  $N<\begin{matrix}CCl\cdot CCl\\ CCl_2\cdot CCl\end{matrix}$, is obtained when phosphorus pentachloride acts on dichloromaleinimide (2 mols.) at 160°, and boils at 90·5° under a pressure of 10 mm.; its vapour is very irritating. Boiling water converts the substance into dichloromaleinimide, which is also produced by the action of alcohol. Reduction with sodium amalgam gives rise to tetrachloropyrroline, which Ciamician and Silber obtained on reducing perchloropyrrocoll (Abstr., 1884, 292); the tetrachloro-derivative forms lustrous leaflets, and melts and decomposes at 110°. Pentachloropyrroline is also produced when phosphorus pentachloride (4 mols.) acts on succinimide in chloroform.

The authors conclude their paper with a general discussion of the results. M. O. F.

Electro-syntheses in the Pyridine and Quinoline Groups. By Felix B. Ahrens (*Chem. Centr.*, 1896, i, 1125—1127; from *Zeit. Elektrotechn. u. Elektrochem.*, 1896, 2, 577—581).—By the electrolysis of a solution of pyridine in 10 parts of 10 per cent. sulphuric acid, employing a lead cathode and a current density of 14 ampères per 100 sq. cm., the temperature rises to 55°, hydrogen is at length evolved, and eventually 95 per cent. of the theoretical yield of piperidine is obtained. No diaphragm is necessary, as the oxygen evolved at the anode has no action either on pyridine or piperidine. Picoline is similarly reduced to pipecoline. After frequent use, the lead cathodes become inoperative, and hydrogen is liberated without reduction. A solution of pyridine in concentrated sulphuric acid is not reduced at the cathode, but sulphur is separated and hydrogen sulphide evolved. On diluting this solution with water, and electrolysing with a low current density, using a platinum cathode, a brown, amorphous powder insoluble in acids, alkalis, water, and organic solvents, and of the composition represented by the formula $C_7H_{16}NSO_{41}$, separates, on the cathode.

The solution of a nitrosopiperidine base in 20 parts of 10 per cent. sulphuric acid is placed in the cathode vessel and this is immersed in dilute sulphuric acid, the electrodes being of lead. A current density of 14 ampères per 100 sq. cm. at 5—6 volts. is used, and the operation carried on until hydrogen is freely evolved at the cathode, where the temperature of the liquid rises to 45—50°. Nitrosopiperidine yields pyridine and *piperylhydrazine*, $C_5NH_{10}\cdot NH_2$, a colourless, very pungent liquid boiling at 145—146°. The hydrochloride forms fine crystals, melts at 163—164°, and is easily soluble in water and alcohol; the hydrobromide is obtained in white crystals melting at 174—175°; the hydriodide crystallises in needles. The *platinochloride* crystallises in small, orange needles, sinters at 110° and froths at 116°. The hydrochloride of the benzoyl derivative, $C_5H_{11}N_2Bz,HCl$, obtained by the action of benzoic chloride on piperylhydrazine, in ethereal solution, is a white precipitate melting at 183—184° and easily soluble in water and alcohol. The free base, liberated by treatment with ammonia, crystallises in lustrous leaflets and melts at 195°.

Nitroso-α-pipecoline is similarly reduced to ammonia, α-pipecoline and *piperylmethylhydrazine*, $C_5NH_9Me\cdot NH_2$, a pungent, colourless liquid boiling at 162—165°, forming a *hydrochloride* which crystallises in white needles melting at 175°, and a *benzoyl* derivative melting at 165—166°. The *mercurochloride* forms compact crystals, which, on warming with excess of potassium hydroxide until the liquid becomes grey from separation of mercury, yields *αα-dimethyldipiperyltetrazone*, $N_2(C_5NH_9Me)_2$, which forms colourless needles or compact crystals melting at 56—57°.

Nitrosoaldehydocopellidine, on reduction by electrolysis, gives *methylethylpiperylhydrazine*, $C_5NH_8MeEt\cdot NH_2$, a very pungent liquid boiling at about 205°.

If a solution of nitrosopiperidine in 10 parts of 30 per cent. sulphuric acid and a little alcohol is placed in the porous anode vessel, this immersed in 30 per cent. sulphuric acid, and electrolysis carried on with platinum electrodes, employing a current density of 11—24 ampères per 100 sq. cm., at 4—5 volts., the temperature of the anode solution rises and the anode is attacked. *Dipiperidyl*, $C_{10}H_{20}N_2$, is produced and forms fine, colourless crystals melting at 96—97°, soluble in water, alcohol, ether, benzene, light petroleum, and chloroform, and instantly reducing silver or gold solutions. The *monobenzoyl* derivative is a colourless syrup, and its *hydrochloride* a white, crystalline precipitate. Attempts to oxidise piperidine in sulphuric acid solution, employing a current density of 14 ampères per 100 sq. cm. at 3·7—4·6 volts., failed.

By electrolysing a solution of quinoline in 20 parts of 10 per cent. sulphuric acid in the same way as nitrosopiperidine, but employing a current density of 17 ampères per 100 sq. cm. at 5·5 volts., tetrahydroquinoline, C_9NH_{11}, dihydroquinoline, $(C_9NH_9)_2$, and the polymeric dihydroquinoline, $(C_9NH_9)_3$, which sinters at 58° and melts below 80° to a clear, viscous liquid, are formed. By the action of hydrochloric acid and sodium nitrite, this compound forms the nitroso-derivative, $(C_9NH_8\cdot NO)_3$, as a greenish-yellow precipitate, which, on warming with tin and hydrochloric acid, is partially reduced to tetrahydroquinoline. A red liquid is formed at the anode which yields lustrous, brown needles and is capable of dyeing wool yellowish-green directly in sulphuric acid solution.

On electrolysis in the same way as quinoline, quinaldine yields *tetrahydroquinaldine*, $C_{10}H_{13}N$, and *dihydroquinaldine*, $(C_{10}H_{11}N)_3$, a white, amorphous powder which, on melting, behaves like the corresponding dihydroquinoline, and resembles it also in its solubility in the various reagents. It forms a yellow nitroso-compound, $(C_{10}H_{10}N{\cdot}NO)_3$.

E. W. W.

Mercuropiperidine Compounds. By F. Cerdelli (*Gazzetta*, 1897, 27, i, 18—23).—On saturating a hot, aqueous solution of piperidine sulphate with yellow mercuric oxide, filtering, and allowing to cool, *mercuropiperidine sulphate*, $Hg(C_5H_{11}N)_2SO_4$, separates in lustrous, colourless prisms containing $6H_2O$, of which $5H_2O$ is lost over sulphuric acid; it decomposes at 100°, and when its aqueous solution is treated with barium carbonate, carbonic anhydride and piperidine are liberated, and *mercuropiperidine hydroxide*, $Hg(C_5H_{11}N{\cdot}OH)_2$, remains in solution. The hydroxide reacts with potassium iodide in accordance with the following equation, $Hg(C_5H_{11}N{\cdot}OH)_2 + 2KI = 2C_5H_{11}N + HgI_2 + 2KHO$.

A double *compound* of the composition $3Hg(C_5H_{11}NCl)_2,HgCl_2$, separates in colourless needles on cooling a solution of mercuric chloride in piperidine; it is decomposed by water, and on treatment with hydrogen sulphide yields piperidine hydrochloride and mercuric sulphide. A *compound* of the composition $2Hg(C_5H_{11}NCl)_2,HgCl_2$ separates as a white, amorphous powder on mixing aqueous solutions of mercuropiperidine sulphate and sodium chloride. W. J. P.

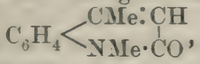
Organo-mercuric Compounds derived from α-Picoline. By G. Garbarini (*Gazzetta*, 1897, 27, i, 23—27).—The author has prepared salts of mercuro-α-picoline analogous to those of mercuropyridine obtained by Pesci (Abstr., 1896, i, 388).

Mercuro-α-picoline sulphate, $Hg(C_6H_7N)_2SO_4$, separates in colourless needles containing $3{\cdot}5H_2O$, on cooling a solution of mercuric sulphate in aqueous α-picoline solution; it loses its water over sulphuric acid, and decomposes at about 200° without melting. The *hydroxide*, obtained in solution by decomposing the sulphate with barium carbonate, reacts with potassium iodide similarly to mercuropiperidine hydroxide (compare preceding abstract). Mercuric chloride dissolves in α-picoline with development of heat, and on cooling the saturated solution, lustrous, colourless needles of a double *compound* of the composition $5Hg(C_6H_7NCl)_2,HgCl_2$, which melts at 170—172°, are deposited. Microscopic, colourless needles of a double *compound* of the composition $Hg(C_6H_7NCl)_2,HgCl_2$ separate on mixing alcoholic solutions of α-picoline and mercuric chloride. W. J. P.

Addition of Methylic Iodide to Methylquinaldone. By Ludwig Knorr (*Ber.*, 1897, 30, 922—926).—When methylquinaldone is heated at 100° with methylic iodide, the pseudomethiodide is formed, identical with the methiodide of γ-methoxyquinaldine (Conrad and Eckhardt, Abstr., 1889, 519). Methylquinaldone, therefore, behaves towards methylic iodide in an analogous manner to antipyrine, which it also resembles in constitution. A. H.

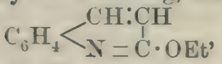
An Additive Compound of Methylquinaldone and Benzoic Chloride. By Ludwig Knorr and Paul Rabe (*Ber.*, 1897, 30, 927—928. Compare the foregoing abstract).—Methylquinaldone also resembles antipyrine in its behaviour towards benzoic chloride, forming an unstable *additive compound*, which crystallises in small, faintly-red needles. When rapidly heated, it melts at 112°, then again solidifies, and when further heated melts at 158—160°. If slowly heated, it softens at 115—120° and melts at 160—161°. In its reactions, it closely resembles antipyrine chlorobenzoylate (this vol., i, 110), and it is probable that the two substances have a similar constitution. Aqueous soda converts it into methylquinaldone, sodium chloride and benzoate being formed. A. H.

Behaviour of the Oxygen Ethers of Carbostyril and 2′-Hydroxy-4′-lepidine towards Alkyl Halogen Derivatives. By LUDWIG KNORR (*Ber.*, 1897, **30**, 929—933. Compare the two foregoing abstracts).—The nitrogen ethers of the α-quinolones, such as methyllepidone,

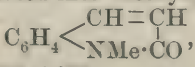


$C_6H_4<\begin{array}{l}CMe{:}CH\\ NMe\cdot CO\end{array}$, do not yield methiodides when heated with methylic iodide, and thus differ from the corresponding derivatives of γ-quinaldine and 1′-phenyl-3′-methylpyrazolone.

The oxygen ethers of the α-quinolones, on the other hand, are converted by methylic iodide into the nitrogen methyl ethers, the change taking place completely and rapidly on warming, slowly in the cold. Thus, when 2′-ethoxyquinoline,

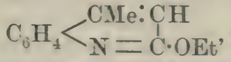


$C_6H_4<\begin{array}{l}CH{:}CH\\ N=C\cdot OEt\end{array}$, is heated with methylic iodide, it is converted into methylquinolone,



$$C_6H_4<\begin{array}{l}CH=CH\\ NMe\cdot CO\end{array},$$

Ethoxylepidine,

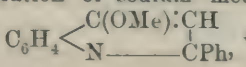


$C_6H_4<\begin{array}{l}CMe{:}CH\\ N=C\cdot OEt\end{array}$, and methoxylepidine, when treated in a similar manner, yield methyllepidone.

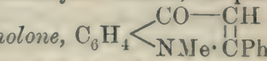
It seems probable that quaternary iodides are formed as intermediate products in these reactions, but none of these has yet been isolated. The reaction is otherwise strictly analogous to that which occurs with antipyrine, the pseudomethiodide of which is unstable, and with the alkyl-4′-quinolones, the pseudomethiodides of which are stable, and can readily be prepared. A. H.

Behaviour of 4′-Methoxy-2′-phenylquinoline towards Methylic Iodide. By LUDWIG KNORR and EDUARD FERTIG (*Ber.*, 1897, **30**, 937—940. Compare preceding abstract).—4′-Methoxy-2′-phenylquinoline resembles 2′-methoxylepidine in being directly converted by methylic iodide into the isomeric 2′-phenyl-1′-methyl-4′-quinolone, without the formation of a stable intermediate product. This difference between the behaviour of this substance and of 4′-methoxyquinoline is probably due to the acidifying effect of the phenyl group.

4′-*Chloro-2′-phenylquinoline*, obtained by the action of phosphorus pentachloride on 2′-phenyl-4′-quinolone, melts at 63—64°; when treated with a solution of sodium methoxide, it yields 4′-*methoxy-2′-phenylquinoline*,



$C_6H_4<\begin{array}{l}C(OMe){:}CH\\ N\text{———}CPh\end{array}$, which crystallises in needles melting at 69—70°, and is slowly volatile with steam. When this substance is heated with methylic iodide, it passes into the isomeric *2′-phenyl-*1′*-methyl-*4′*-quinolone*,



$C_6H_4<\begin{matrix}CO—CH \\ NMe\cdot CPh\end{matrix}$, which crystallises in lustrous plates melting at 85°, and is not volatile with steam.

A. H.

1-Quinolyloxyacetic Acid. By Oskar Nagel (*Monatsh.*, 1897, **18**, 31—43).—When an alcoholic solution of 1-hydroxyquinoline (1 mol.) is added to alcoholic sodium ethoxide (2 mols.), the product dissolved by the gradual addition of water, an alcoholic solution of chloracetic acid added, and the whole heated on the water bath for 12 hours, 50 per cent. of the hydroxyquinoline can be recovered unchanged, but 1-*quinolyloxyacetic acid*, $C_9NH_6\cdot O\cdot CH_2\cdot COOH$, can be isolated from the product of the action. This acid melts at 176° (uncorr.), loses carbonic anhydride when further heated, and yields a *dibromo*-derivative which melts at 203°. Its *silver*, $C_{11}H_8NO_3Ag$, *barium* $(C_{11}H_8NO_3)_2Ba + 3H_2O$, and *potassium*, $C_{11}H_8NO_3K + H_2O$, salts were prepared; also the *hydrochloride*, $C_{11}H_9NO_3,HCl$, melting at 216°; the orange-yellow *platinochloride* $(C_{11}H_9NO_3)_2,H_2PtCl_6 + 2H_2O$, melting and decomposing at 210°; the *stannochloride*, $C_{11}H_9NO_3,HSnCl_3 + H_2O$; a compound with mercuric chloride, $(C_{11}H_9NO_3)_2,HgCl_2 + 3H_2O$; the *hydriodide*, $C_{11}H_9NO_3,HI + 2H_2O$, melting at 193°; and the *sulphate*,

$$C_{11}H_9NO_3,H_2SO_4 + 2H_2O,$$

melting at 115°. The acid character is more pronounced than the basic.

C. F. B.

Synthesis of Isoquinoline and its Derivatives. By Cæsar Pomeranz (*Monatsh.*, 1897, **18**, 1—5. Compare Abstr., 1894, i, 552).—The derivatives described were obtained by condensing a derivative of benzaldehyde or benzophenone with amidoacetal, dissolving the product in strong sulphuric acid, the mixture being kept cool with ice, allowing it to remain for 2 hours, and then adding half the volume of phosphorus oxychloride and heating for ¼-hour over a naked flame. Of the first compound described, the yield was 20 per cent. of the theoretical; of the last two, enough was not obtained for a combustion.

1-*Methylisoquinoline*, from orthomethylbenzaldehyde, boils at 258°; the red *platinochloride*, $(C_9NH_6Me)_2,H_2PtCl_6 + 2H_2O$, and yellow *picrate*, melting at 204—205°, were prepared. 3-*Methylisoquinoline*, from paramethylbenzaldehyde, melts at 83° and boils at 263—264° (uncorr.); the *platinochloride* and *picrate*, the latter melting at 212°, resemble those of the 1-methyl compound in appearance and composition. 1-*Chlorisoquinoline*, from orthochlorobenzaldehyde, melts at 55°, and yields a red *platinochloride*, $(C_9NH_6Cl)_2,H_2PtCl_6$. 1′-*Phenylisoquinoline*, from benzophenone, melts at 87—88°; the *platinochloride*,

$$(C_9NH_6Ph)_2,H_2PtCl_6,$$

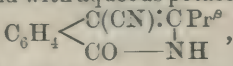
is red.

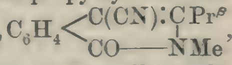
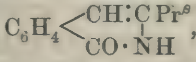
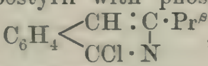
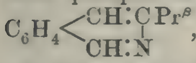
C. F. B.

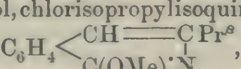
Synthesis of 3′-Isopropylisoquinoline and of 3′-Butylisoquinoline. By J. N. Lehmkuhl (*Ber.*, 1897, **30**, 889—897).—Using Gabriel and Neumann's method for the preparation of alkylated derivatives of isoquinoline, the following compounds have been isolated.

ψ-Di-isobutyrylorthocyanobenzylic cyanide,

$$CN\cdot C_6H_4\cdot C(CN){:}CPr^{\beta}\cdot O\cdot COPr^{\beta},$$

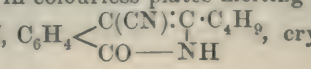
is prepared by condensing orthocyanobenzylic cyanide and isobutyric anhydride; when crystallised from alcohol, it contains 1 mol. EtOH and melts at 140°; on hydrolysing this compound with aqueous potassium hydroxide, 3′:4′-*isopropylcyanoisocarbostyril*,  $C_6H_4{<}\begin{matrix}C(CN){:}CPr^{\beta}\\ CO\text{——}NH\end{matrix}$, is produced, a compound crystallising from alcohol in pale yellow needles, and melting with partial decomposition at 227—229°; as a bye-product in this reaction, there is also formed *α-orthodicyano-β-ethoxyamenylbenzene,* $CN\cdot C_6H_4\cdot C(CN){:}CPr^{\beta}\cdot OEt$, a substance crystallising from alcohol in well formed needles melting at 91°.

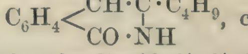
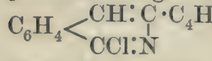
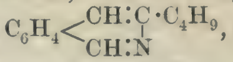
By the action of methylic iodide on 3′:4′-isopropylcyanoisocarbostyril, 2′:3′:4′-*methylisopropylcyanoisocarbostyril,*  $C_6H_4{<}\begin{matrix}C(CN){:}CPr^{\beta}\\ CO\text{——}NMe\end{matrix}$, is produced, which crystallises from alcohol in colourless needles melting at 200°—210°; both from the methyl derivative as well as from the unmethylated compound, the cyano-group can be eliminated by hydrolysis with concentrated sulphuric acid, yielding 3′-*isopropylisocarbostyril,*  $C_6H_4{<}\begin{matrix}CH{:}CPr^{\beta}\\ CO\cdot NH\end{matrix}$, which crystallises from alcohol in colourless crystals melting at 186—189°, and the corresponding 2′-*methyl* derivative, which forms colourless needles melting at 184—186°. On treating 3′-isopropylisocarbostyril with phosphorus oxychloride, 1′:3′-chlorisopropylisoquinoline,  $C_6H_4{<}\begin{matrix}CH{:}C\cdot Pr^{\beta}\\ CCl\cdot N\end{matrix}$, is formed; this is a colourless liquid boiling at 292—293° (748 mm.), and on reduction with phosphorus and hydriodic acid yields 3′-*isopropylisoquinoline,*  $C_6H_4{<}\begin{matrix}CH{:}CPr^{\beta}\\ CH{:}N\end{matrix}$, a colourless liquid boiling at 264—266° (771 mm.), and forming a *platinochloride* consisting of yellow needles melting at 180—182°, an *aurochloride* crystallising in needles, and a yellow *picrate.*

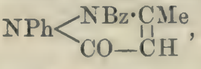
On treatment with sodium and methylic alcohol, chlorisopropylisoquinoline yields 1′:3′-*methoxyisopropylisoquinoline,*  $C_6H_4{<}\begin{matrix}CH{=\!=}CPr^{\beta}\\ C(OMe){:}N\end{matrix}$, a colourless oil boiling at 268—270° (772 mm.), and having slightly basic properties; the corresponding *ethoxy*-derivative boils at 283—285° (771 mm.), the *phenoxy*-compound is a dark brown oil which does not distil unchanged; all these compounds yield yellow, crystalline *platinochlorides.*

On condensing orthocyanobenzylic cyanide with valeric anhydride, *ψ-divalerylorthocyanobenzylic cyanide,*

$$CN\cdot C_6H_4\cdot C(CN){:}C(C_4H_9)\cdot O\cdot CO\cdot C_4H_9,$$

is formed; this crystallises from alcohol in colourless plates melting at 153—154°. 3′:4′-*Butylcyanoisocarbostyril,*  $C_6H_4{<}\begin{matrix}C(CN){:}C\cdot C_4H_9\\ CO\text{——}NH\end{matrix}$, crystallises from alcohol in pale yellow needles melting at 227—229°, a similar bye-product as in the former case, namely, *ortho-a-dicyano-β-ethoxyhexenylbenzene*, $CN\cdot C_6H_4\cdot C(CN){:}C(C_4H_9)\cdot OEt$, being also formed; after recrystallisation from alcohol, this melts at 72°.

3′-*Butylisocarbostyril*,  $C_6H_4<\begin{array}{l}CH\cdot C\cdot C_4H_9\\ CO\cdot NH\end{array}$, crystallises in brown plates melting at 138—139°; the liquid 1′ : 3′-*chlorobutylisoquinoline*,  $C_6H_4<\begin{array}{l}CH{:}C\cdot C_4H_9\\ CCl{:}N\end{array}$, boils at 298—300° (758 mm.), and gives a yellow, crystalline *platinochloride*; on reduction, the chloro-compound yields 3′-*butylisoquinoline*,  $C_6H_4<\begin{array}{l}CH{:}C\cdot C_4H_9\\ CH{:}N\end{array}$, a slightly coloured oil boiling at 278° (745 mm.), which has only feebly basic properties, but yields, however, a well-defined crystalline *platinochloride*. J. F. T.

Constitution of Acid Derivatives of 1-Phenyl-3-methyl-5-pyrazolone. By FRIEDRICH STOLZ (*J. pr. Chem.*, 1897 [ii], **55**, 145—171).—The compounds obtained by Nef, Himmelbauer, and others, by the action of benzoic chloride, acetic chloride, benzylic chloride, ethylic chloroformate, and ethylic acetate on 1 : 3-phenylmethyl-5-pyrazolone in the presence of aqueous sodium hydroxide, and thought by them to be 2-derivatives of the pyrazolone with formulæ such as  $NPh<\begin{array}{l}NBz\cdot CMe\\ CO—CH\end{array}$, are shown to be in reality 5-derivatives of the isomeric pyrazole, having the formulæ $NPh<\begin{array}{l}N=\!=\!=CMe\\ C(OBz){:}CH\end{array}$, &c. In the first place, the benzoyl derivative yields, by direct addition in benzene solution, a *methiodide* melting and decomposing at 188°, and this is readily converted, by warming with dilute sodium hydroxide, into antipyrine, benzoic acid, and hydriodic acid; it would be difficult to reconcile this ready formation of antipyrine with the first of the two formulæ given above. Secondly, they do not exhibit the characteristic reactions of antipyrine (colorations with ferric chloride and with nitrous acid, sparing solubility in ether and light petroleum), but have rather the character of alkoxy-compounds. It may be added that 4-derivatives of pyrazolone are often simultaneously formed in the reaction. There seems, however, to be no way of getting 2-derivatives by the direct action of the acid chlorides, &c., on phenylmethylpyrazolone. Nor can these be synthesised by the action of acetyl-, formyl-, or benzoyl-phenylhydrazine on ethylic acetoacetate; such action in the presence of phosphorus trichloride results in the formation of the diacidylhydrazine, together with 1 : 3-phenyl-methyl-5-pyrazolone, and usually some 1 : 5-phenylmethyl-3-pyrazolone and other products. They can, however, be obtained by acting on a 5-alkoxypyrazole derivative and then hydrolysing the alkoxy-group with alkali.

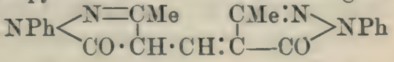
Himmelbauer's 1 : 2 : 3-*phenylbenzylmethyl* 5 *pyrazolone*, melting at 134—136°, is in reality the 1 : 4 : 3 : 5 compound, and had already been discovered twice. The 1 : 2 : 3 : 5 compound, $C_{17}H_{16}N_2O,H_2O$, can, however, be obtained by heating phenylmethylpyrazolone with benzylic chloride for 12 hours at 120°; when anhydrous, it melts at 119°.

1-*Parethoxyphenyl-3-methyl-5-acetoxypyrazole* is obtained by treating ethoxyphenylmethylpyrazolone in alkaline solution with acetic anhydride; it melts at 76°. 4-*Acetyl*-1 : 3-*phenylmethyl-5-pyrazolone* is obtained by boiling commercial "pyrazolone" with acetic anhydride and sodium acetate; it melts at 58°; the acetyl group is removed by boiling with hydrochloric acid, "pyrazolone" being re-formed; it is remarkable that sodium hydroxide does not effect this change.

1 : 3-*Phenylmethyl-5-pyrazolone-2-acetic acid* was obtained by heating phenylmethyl-5-ethoxypyrazole with ethylic iodacetate for 12 hours at 100° and warming the product with aqueous sodium hydroxide; it melts and decomposes at 205—207°; the *ethylic salt* melts at 118°.

1 : 3-*Phenylmethylpyrazole-5-oxyacetic acid* is obtained by adding sodium ethoxide and then ethylic chloracetate to an alcoholic solution of phenylmethylpyrazolone and hydrolysing the ethylic salt thus formed; it melts at 158°; the *methylic* and *ethylic* salts melt at 75° and 47° respectively.

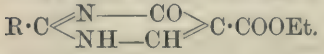
1 : 3 : 4-*Phenyldimethyl-5-pyrazolone-2-acetic acid* (Himmelbauer's 4-acetic acid), obtained by the action of ethylic bromacetate on phenyldimethyl-5-ethoxypyrazole and subsequent hydrolysis of the product, melts and decomposes at 215° (Himmelbauer 190°); the *methylic* salt melts at 112°. 1 : 3 : 4-*Phenyldimethyl-5-pyrazolone-4-acetic acid* (Himmelbauer's 2-acetic acid) is formed, together with the preceding acid, when an alkaline solution of phenyldimethylpyrazolone is boiled for half an hour with chloracetic acid; it melts at 103°; the *methylic* salt melts at 143°, and differs from that of the preceding acid in being insoluble in water, from that of the following acid by its lesser solubility in methylic alcohol. 1 : 3 : 4-*Phenyldimethylpyrazole-5-oxyacetic acid* is obtained by boiling an alcoholic solution of phenyldimethylpyrazolone and sodium ethoxide with ethylic chloracetate and hydrolysing the product; it melts at 141°, its *methylic* salt at 55°.

Among the products of the action of formyl- and of benzoyl-phenylhydrazine on ethylic acetoacetate, there was obtained in both cases an orange-yellow substance melting at 180°. This can also be obtained from "pyrazolone" and formic acid, and it is identical with the products obtained respectively by Knorr from 1 : 3-phenylmethyl-5-pyrazolone with chloroform and alkali, and by Pellizzari from phenylmethylpyrazolone and paraformaldehyde, and also by the loss of water from 1 : 3-phenylmethyl-4-methoxy-5-pyrazolone. Molecular weight-determinations lead to the formula  $\mathrm{NPh}\left\langle\begin{array}{l}\mathrm{N{=}\overset{}{C}Me}\qquad\ \mathrm{CMe{:}N}\\ \quad\ \ |\qquad\qquad\quad |\\ \mathrm{CO{\cdot}CH{\cdot}CH{:}C{-}CO}\end{array}\right\rangle\mathrm{NPh}$ for this substance.

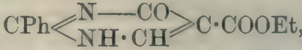
C. F. B.

Compounds of Antipyrine with the Cresols. By GUSTAVE PATEIN and E. DUFAU (*Bull. Soc. Chim.*, 1896, [iii], **15**, 609—610).—*Orthocresol-antipyrine*, $C_6H_4Me{\cdot}OH,C_{11}H_{12}N_2O$, is formed when orthocresol is fused with antipyrine. From alcohol, it crystallises in colourless crystals melting at 60—62°, which are very slightly soluble in water and ether, but more soluble in chloroform. On mixing an alcoholic solution of metacresol with an aqueous solution of antipyrine, an oily liquid separates, which, on standing for some time, deposits crystals of antipyrine, the residual liquid then having the composition corresponding with the union of the two substances in molecular proportion. It is almost odourless, soluble in alcohol and ether, and partially decomposed by water. When allowed to remain over sulphuric acid, it undergoes slow decomposition, antipyrine crystallising out, and the cresol being disengaged in the state of vapour, the composition of the liquid therefore remaining constant. When paracresol is substituted for the meta-compound in the above experiment, analogous results are obtained, an oily compound of 1 mol. of the cresol with 1 mol. of antipyrine being obtained. A. C. C.

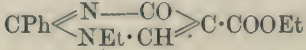
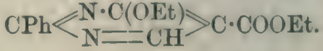
Formation of Pyrimidones. By SIEGFRIED RUHEMANN (*Ber.*, 1897, **30**, 821—823).—Ethylic dicarboxyglutaconate reacts with amidines to produce derivatives of pyrimidone, according to the equation $NH_2\cdot CR\colon NH + (COOEt)_2CH\colon C(COOEt)_2 = CH_2(COOEt)_2 + C_2H_6O +$



$R\cdot C{<}\begin{matrix}N\text{——}CO\\ NH\text{—}CH\end{matrix}{>}C\cdot COOEt.$

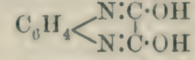
Ethylic phenylpyrimidonecarboxylate,  $CPh{<}\begin{matrix}N\text{——}CO\\ NH\cdot CH\end{matrix}{>}C\cdot COOEt$, is obtained by heating an alcoholic solution of benzamidine hydrochloride, sodium ethoxide, and ethylic dicarboxyglutaconate. It crystallises in colourless needles melting at 214°, and is only very sparingly soluble in alkalis. The free *acid* crystallises in small prisms, melts at 265°, and is sparingly soluble in boiling water. The *silver* salt has the composition $C_{11}H_6Ag_2N_2O_3$. Ethylic phenylpyrimidonecarboxylate dissolves in warm, aqueous ammonia, yielding a solution from which silver nitrate precipitates a gelatinous *silver* salt,

$$C_{13}H_{11}AgN_2O_3.$$

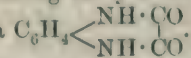
When this is heated with ethylic iodide, it is converted into an ethyl ether, which appears to be a mixture of the two possible isomeric ethers,  $CPh{<}\begin{matrix}N\text{——}CO\\ NEt\cdot CH\end{matrix}{>}C\cdot COOEt$ and  $CPh{<}\begin{matrix}N\cdot C(OEt)\\ N\text{===}CH\end{matrix}{>}C\cdot COOEt.$

A. H.

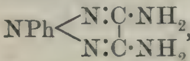
Action of Ethylic Oxalate on Aromatic Amines. II. By RICHARD E. MEYER (*Ber.*, 1897, **30**, 768—770. Compare this vol., i, 45).—The dioxyquinoxaline prepared by the author from ethylic oxalate, and orthotolylenediamine [1 : 3 : 4] is now found to be identical with the compound obtained by Hinsberg from oxalic acid on condensation with the same base. Hinsberg assigns the formula

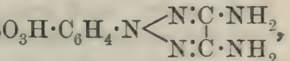


$$C_6H_4{<}\begin{matrix}N\colon C\cdot OH\\ |\\ N\colon C\cdot OH\end{matrix}$$

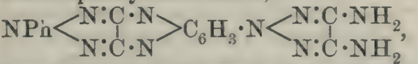
to this substance, whilst its preparation from ethylic oxalate, and the fact that ethylic alcohol is eliminated during the process of condensation, would seem to indicate the formula  $C_6H_4{<}\begin{matrix}NH\cdot CO\\ |\\ NH\cdot CO\end{matrix}$. The general reactions of the substance can be explained by the use of either formula. J. F. T.

Diamidophenylosotriazole. By JOHANNES THIELE and KARL SCHLEUSSNER (*Annalen*, 1897, **295**, 129—172).—*Oxalenphenylhydrazidamidoxime*, $\mathrm{NHPh\cdot N{:}C(NH_2)\cdot C(NH_2){:}NOH}$, obtained by heating a concentrated alcoholic solution of dicyanophenylhydrazine with an aqueous solution of hydroxylamine (1 mol.), crystallises from ethylic acetate in lustrous scales melting at 174°; the solution in alkalis rapidly becomes dark red, and a red coloration is also developed with ferric chloride. The *acetyl* derivative, which is likewise readily oxidised, crystallises from alcohol in scales and melts at 146°.

Diamidophenylosotriazole,  $\mathrm{NPh}\Big<\begin{matrix}\mathrm{N{:}C\cdot NH_2}\\ \mathrm{N{:}C\cdot NH_2}\end{matrix}$, is produced when the foregoing oxime is heated with 6 parts of water at 150° during 2 hours, and crystallises from water in long, colourless needles melting at 143°; the aqueous solution is neutral, and exhibits strong reducing action, a deep indigo-blue coloration being developed by ferric chloride and bromine water, whilst a solution in hydrochloric acid stains fir-wood deep red. When alkaline solutions are heated at 150—200°, a reddish-brown, infusible condensation product is formed, insoluble in ordinary solvents; fuming hydrochloric acid at 200° completely decomposes the base, and the production of phenylprozane, $\mathrm{NH_2\cdot NPh\cdot NH_2}$, could not be established. The *hydrochloride* of diamidophenylosotriazole crystallises from water or dilute alcohol in leaflets, and melts at 210°, whilst the *sulphate* crystallises in plates; the *picrate* crystallises in fascicular aggregates of needles and melts at 153°. The *silver nitrate* compound crystallises in colourless leaflets and melts and totally decomposes at 150°; the solutions rapidly become blue.

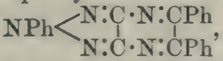
Diamidophenylosotriazolesulphonic acid,  $\mathrm{SO_3H\cdot C_6H_4\cdot N}\Big<\begin{matrix}\mathrm{N{:}C\cdot NH_2}\\ \mathrm{N{:}C\cdot NH_2}\end{matrix}$, obtained by dissolving the base in 8 or 10 per cent. fuming sulphuric acid, forms colourless needles very sparingly soluble in water; the solution, however, develops an intense brown coloration with bromine, the liquid, whilst indifferent towards mineral acids, being decolorised by alkalis. The *sodium* salt crystallises in colourless plates, and the *ammonium* salt separates from water in colourless needles.

The *azine* of diamidophenylosotriazole,



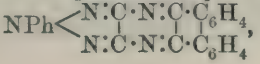
$$\mathrm{NPh}\Big<\begin{matrix}\mathrm{N{:}C\cdot N}\\ \mathrm{N{:}C\cdot N}\end{matrix}\Big>\mathrm{C_6H_3\cdot N}\Big<\begin{matrix}\mathrm{N{:}C\cdot NH_2}\\ \mathrm{N{:}C\cdot NH_2}\end{matrix},$$

is a blue, amorphous substance, obtained by oxidising the triazole in 1 per cent. hydrochloric acid with ferric chloride; stannous chloride and hydrochloric acid reduce it to the *leuco*-compound, which crystallises in colourless needles and melts, when anhydrous, at 175°. The *quinoxaline* from diamidophenylosotriazole and benzile,

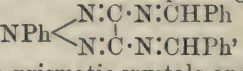


$$\mathrm{NPh}\Big<\begin{matrix}\mathrm{N{:}C\cdot N{:}CPh}\\ \mathrm{N{:}C\cdot N{:}CPh}\end{matrix},$$

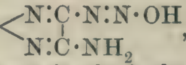
crystallises from glacial acetic acid in deep red needles, and melts at 217°; concentrated sulphuric acid dissolves it with a deep violet coloration, which becomes red on dilution with water. The *quinoxaline* from diamidophenylosotriazole and phenanthraquinone,



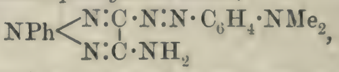
$$\mathrm{NPh}\Big<\begin{matrix}\mathrm{N{:}C\cdot N{:}C\cdot C_6H_4}\\ \mathrm{N{:}C\cdot N{:}C\cdot C_6H_4}\end{matrix},$$

crystallises from chloroform in needles, and melts at 289°; the solution in concentrated sulphuric acid is deep indigo blue. *Dibenzylidenediamidophenylosotriazole,*  $\mathrm{NPh}\left<\begin{array}{l}\mathrm{N{:}C\cdot N{:}CHPh}\\ \quad\;\mathrm{|}\\ \mathrm{N{:}C\cdot N{:}CHPh}\end{array}\right.$, separates from glacial acetic acid in yellowish, prismatic crystals, and melts at 162°; *dihydroxybenzylidenediamidophenylosotriazole* crystallises in yellow needles and melts at 210°.

The *monacetyl* derivative of diamidophenylosotriazole dissolves more readily in water than the acetyl derivative, and crystallises in needles melting at 186°; when prepared in the ordinary manner, it is associated with the diacetyl derivative, and is therefore more conveniently obtained by heating that compound with diamidophenylosotriazole at 200—210° during 4 hours. The *diacetyl* derivative forms colourless, prismatic crystals and melts at 206°. The *dibenzoyl* derivative melts at 242°.

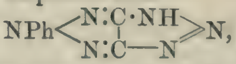
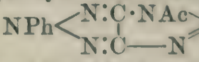
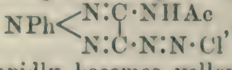
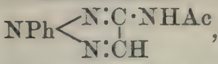
Amidodiazophenylosotriazole,  $\mathrm{NPh}\left<\begin{array}{l}\mathrm{N{:}C\cdot N{:}N\cdot OH}\\ \quad\;\mathrm{|}\\ \mathrm{N{:}C\cdot NH_2}\end{array}\right.$, is obtained by adding a solution of diamidophenylosotriazole hydrochloride to a cold solution of free nitrous acid, an amorphous, greenish-yellow, insoluble compound being produced when this order of procedure is reversed; the *picrate* crystallises in needles, and melts and decomposes at 121°.

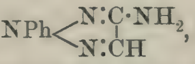
Dimethylanilineazoamidophenylosotriazole,

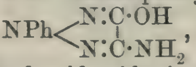
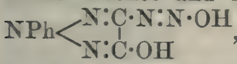
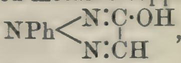


$$\mathrm{NPh}\left<\begin{array}{l}\mathrm{N{:}C\cdot N{:}N\cdot C_6H_4\cdot NMe_2}\\ \quad\;\mathrm{|}\\ \mathrm{N{:}C\cdot NH_2}\end{array}\right.,$$

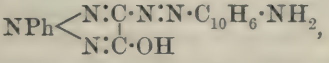
crystallises from alcohol in red needles and melts and decomposes at 243°; it dyes wool orange yellow, and forms an intense cochineal red solution with concentrated sulphuric acid.

Phenylosotriazoleazimide,  $\mathrm{NPh}\left<\begin{array}{l}\mathrm{N{:}C\cdot NH}\\ \quad\;\mathrm{|}\\ \mathrm{N{:}C\text{—}N}\end{array}\right>\mathrm{N}$, is formed when a solution of amidodiazophenylosotriazole is heated on the water bath with sodium acetate; it crystallises from water in colourless needles, becomes brown at 130—140° and when exposed to air is insoluble in petroleum, and melts at 147°. The substance is indifferent towards potassium permanganate and an ammoniacal solution of silver nitrate, and undergoes no change when treated with cold dilute mineral acids; hot 50 per cent. sulphuric acid, however, effects a rupture of the azimide ring, a result which is also brought about under the influence of acetic chloride, the acetyl derivative of amidodiazophenylosotriazole being produced. The *acetyl* derivative of the azimide,  $\mathrm{NPh}\left<\begin{array}{l}\mathrm{N{:}C\cdot NAc}\\ \quad\;\mathrm{|}\\ \mathrm{N{:}C\text{——}N}\end{array}\right>\mathrm{N}$, is prepared by diazotising the monacetyl derivative of diamidophenylosotriazole, and treating the liquid with a concentrated solution of sodium acetate; it is colourless, and explodes at 160°. Whilst phenylosotriazoleazimide is relatively stable towards mineral acids, boiling acetic acid decomposes the acetyl derivative, forming the *acetyl* derivative of amidodiazophenylosotriazole chloride,  $\mathrm{NPh}\left<\begin{array}{l}\mathrm{N{:}C\cdot NHAc}\\ \quad\;\mathrm{|}\\ \mathrm{N{:}C\cdot N{:}N\cdot Cl}\end{array}\right.$, which melts and decomposes at 150—155°, and rapidly becomes yellow and loses hydrogen chloride when exposed to air; mineral acids convert it into the acetyl derivative of phenylosotriazoleazimide, and hot caustic soda gives rise to phenylosotriazoleazimide. The *acetyl* derivative of amidophenylosotriazole,  $\mathrm{NPh}<\begin{array}{l}\mathrm{N{:}C{\cdot}NHAc}\\ \mathrm{N{:}CH}\end{array}$, is obtained by treating the acetyl derivative of phenylosotriazoleazimide with boiling alcohol, aldehyde and nitrogen being eliminated; it crystallises in colourless needles and melts at 166°.

Amidophenylosotriazole,  $\mathrm{NPh}<\begin{array}{l}\mathrm{N{:}C{\cdot}NH_2}\\ \mathrm{N{:}CH}\end{array}$, is prepared from the acetyl derivative, and crystallises from hot water in long, colourless needles, melting at 70°; it behaves as a feeble reducing agent towards ammoniacal silver nitrate, and is coloured pale blue by ferric chloride, probably owing to contamination with diamidophenylosotriazole.

Amidohydroxyphenylosotriazole,  $\mathrm{NPh}<\begin{array}{l}\mathrm{N{:}C{\cdot}OH}\\ \mathrm{N{:}C{\cdot}NH_2}\end{array}$, is a bye-product in the preparation of oxalenphenylhydrazidamidoxime, occurring in the residual alkaline liquid after removing diamidophenylosotriazole; it crystallises from water in long, colourless needles, and melts and decomposes at 181°. The aqueous solution is acidic, and stains a fir splint of an intense reddish-yellow; ferric chloride produces a beautiful, violet colouring matter. The *benzylidene* derivative crystallises from dilute alcohol and melts at 173°. *Diazohydroxyphenylosotriazole,*  $\mathrm{NPh}<\begin{array}{l}\mathrm{N{:}C{\cdot}N{:}N{\cdot}OH}\\ \mathrm{N{:}C{\cdot}OH}\end{array}$, is prepared by adding a dilute alcoholic solution of hydroxyamidophenylosotriazole to a well-cooled solution of nitrous acid; it is a very unstable substance, and in a few days loses the property of combining with sodium β-naphtholdisulphonate. When the solution in sulphuric acid is treated with finely-divided metallic copper, nitrogen is eliminated, and *hydroxyphenylosotriazole,*  $\mathrm{NPh}<\begin{array}{l}\mathrm{N{:}C{\cdot}OH}\\ \mathrm{N{:}CH}\end{array}$, is produced; it crystallises from hot water in long, colourless needles, and melts at 124°.

β-Naphthylamidazohydroxyphenylosotriazole,



$$\mathrm{NPh}<\begin{array}{l}\mathrm{N{:}C{\cdot}N{:}N{\cdot}C_{10}H_6{\cdot}NH_2}\\ \mathrm{N{:}C{\cdot}OH}\end{array},$$

is obtained from diazohydroxyphenylosotriazole and β-naphthylamine; it is brownish-red, and dissolves in concentrated sulphuric acid with an indigo-blue coloration.

Cyanosemicarbazide, $C_2(NH_2)_2(N{\cdot}NH{\cdot}CO{\cdot}NH_2)_2$, produced when cyanogen in alcoholic solution acts on amidoguanidine, crystallises from water in colourless needles which melt and decompose at 223°; the aqueous solution is acidic, and reduces ammoniacal silver nitrate solution.

Dicyanosemicarbazide, $NH_2{\cdot}C(CN){:}N{\cdot}NH{\cdot}CO{\cdot}NH_2$, obtained from cyanogen and semicarbazide, crystallises in fascicular aggregates of colourless needles, and when heated does not melt, but slowly chars, yielding ammonia and hydrogen cyanide; alkalis dissolve and partly decompose it. The *amidoxime,* $NH_2{\cdot}C(NOH){\cdot}C(NH_2){:}N{\cdot}NH{\cdot}CO{\cdot}NH_2$, obtained by the action of hydroxylamine, crystallises from water in colourless needles; it closely resembles dicyanosemicarbazide, but ferric chloride develops a pale yellow coloration, whilst the oxime becomes dark reddish-brown. The *compound*, $C_3H_5N_5O_2$, is produced when a solution of the oxime in water is heated at 160° during 2 hours and subsequently acidified with acetic acid; it separates from hot water in colourless crystals, and is insoluble in the usual organic solvents. The *compound*, $C_6H_{14}N_8O_7$, which remains in the liquid after the foregoing substance has been precipitated with acetic acid, crystallises in silky, infusible needles; the solution in dilute acetic acid becomes pale red with bromine, the colour being destroyed by mineral acids or by excess of the halogen. It decolorises potassium permanganate immediately, and reduces an ammoniacal solution of silver; mineral acids and alkali carbonates at 140—150° eliminate carbonic anhydride and hydrazine.

Phenylhydrazidoxalhydroxamic acid, $NHPh\cdot NH\cdot CO\cdot CO\cdot NH\cdot OH$ or $NHPh\cdot NH\cdot CO\cdot C(OH){:}NOH$, obtained by the action of hydroxylamine (2 mols.) on ethylic phenylhydrazinoxalate, crystallises from methylic alcohol in colourless scales which melt and decompose at 172°; it is very sparingly soluble in common media, but dissolves in alkalis, and after precipitation with acetic acid melts at 178—180°. Ferric chloride develops a violet-red coloration, and boiling glacial acetic acid completely decomposes the substance, yielding a small quantity of phenylurazole; hot soda converts it into phenylhydrazidooxalic acid. The *acetyl* derivative, $NHPh\cdot NH\cdot CO\cdot C(OH){:}NOAc$, separates from acetic acid in pale yellow crystals, and melts at 147°; when heated with 6 to 8 parts of dimethylamine at about 150°, phenylurazole is formed.

Phenylurazole melts at 262° (Pinner, Abstr., 1887, 1042); the *monosodium* and *sodium* derivatives are crystalline, the diacetyl derivative melts at 162—163° (compare *loc. cit.*), and the *monacetyl* derivative crystallises from water or benzene in colourless needles, and melts at 170°. M. O. F.

3 : 6-Dihydroxyxanthone. By RICHARD MEYER and ALFRED CONZETTI (*Ber.*, 1897, **30**, 969—973).—On fusing fluorescein chloride with potash at 270—280° and acidifying the product, a large quantity of a solid substance separates, which can be resolved into its components by dissolving it in ether and agitating it with a solution of sodium carbonate. On acidifying the alkaline solution and distilling with steam, benzoic acid passes over, and dihydroxybenzoylbenzoic acid (m. p. about 200°) separates from the contents of the distillation flask on cooling.

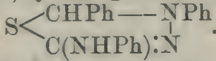
The ethereal solution, besides containing traces of resorcinol, consists for the most part of 2 : 4 : 2′ : 4′-tetrahydroxybenzophenone,

$$C_6H_3(OH)_2\cdot CO\cdot C_6H_3(OH)_2,$$

a substance crystallising from hot water in yellow needles melting at 193—195°, and readily giving up water from the hydroxyls in the ortho-position, passing into 3 : 6 *dihydroxyanthone*, $OH\cdot C_6H_3{<}\genfrac{}{}{0pt}{}{CO}{O}{>}C_6H_3\cdot OH$ [CO : O : OH = 1 : 2 : 4], which separates in slender needles on adding water to its alcoholic solution, and decomposes at 300—350°. Its solution in alkali has a strongly marked blue fluorescence.

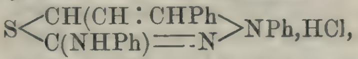
J. F. T.

Action of Aldehydes on Thiosemicarbazides. By Max Busch and Herm. Ridder (*Ber.*, 1897, **30**, 849—855).—Aldehydes react with thiosemicarbazides in very much the same way as with thiocarbazinic acids (Abstr., 1896, i, 190), yielding thiobiazoline derivatives.

Anilidodiphenylthiobiazoline,  $S<\begin{array}{l}CHPh\text{---}NPh\\ C(NHPh):N\end{array}$. A theoretical yield of the *hydrochloride* is obtained when diphenylthiosemicarbazide and benzaldehyde are mixed with alcohol containing hydrogen chloride in solution. The hydrochloride crystallises in greenish-yellow needles, sinters at 232°, and melts at 240°; it is readily soluble in warm alcohol or acetic acid, but insoluble in cold water, and is decomposed on warming. The *base* is best isolated by decomposing the hydrochloride with dilute ammonia, extracting several times with ether, and then adding light petroleum to the ethereal solution. It crystallises in brownish-red aggregates, and is usually contaminated by a sparingly soluble substance, from which it can be mechanically separated. It melts at 105—106°, and dissolves readily in ether or benzene, yielding dark red solutions. Its alcoholic solution is more orange-red, and on warming yields the above-mentioned sparingly soluble compound, $C_{20}H_{15}N_3S$, which melts and decomposes at 280°.

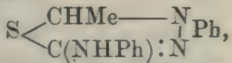
Anilidophenylmetanitrophenylthiobiazoline hydrochloride, obtained from diphenylthiosemicarbazide and metanitrobenzaldehyde, crystallises in small, intensely yellow needles melting at 203°. The *base* has only been obtained in the form of a red oil.

Anilidophenylstyrylthiobiazoline hydrochloride,



$$S<\begin{array}{l}CH(CH:CHPh\\ C(NHPh)\text{==}N\end{array}>NPh,HCl,$$

crystallises in deep yellow needles and melts at 246°.

Anilidophenylmethylthiobiazoline hydrochloride,  $S<\begin{array}{l}CHMe\text{——}NPh\\ C(NHPh):N\end{array}$, crystallises from its ethereal solution in glistening, long, thin plates, melts at 147°, and is easily reconverted into acetaldehyde and diphenylthiosemicarbazide.

Dibenzylaminophenylnitrophenylthiobiazoline hydrochloride, obtained from phenyldibenzylthiosemicarbazide (see this vol., i, 343) and metanitrobenzaldehyde, crystallises in thin, colourless plates, and melts at 108°.

Pulvermacher has previously shown (Abstr., 1894, i, 304) that alkylthiosemicarbazides of the type $NH_2\cdot NH\cdot CS\cdot NHR$ react with aromatic aldehydes to form benzylidene condensation products $R'CH:N\cdot NH\cdot CS\cdot NHR$.

J. J. S.

Use of Potassium Bismuth Iodide in the Preparation of Organic Bases. By Ernst Jahns (*Arch. Pharm.*, 1897, **235**, 151—156).—The author strongly recommends potassium-bismuth iodide solution for the isolation of alkaloids and other organic bases, such as choline and betaine. The solution as prepared by Kraut (*Annalen*, 1882, **210**, 310) is far more delicate as a reagent than those recommended by Dragendorff and by Mangini (*Gazzetta*, 1882, 155). Narceine, solanine, and veratrine, contrary to Classen's statement, yield precipitates with this reagent, creatinine, many tannins, glucosides, and albuminoid substances also give precipitates. It is, therefore, always advisable to first treat the alkaloidal extracts with lead acetate before adding the potassium-bismuth iodide solution. By means of Kraut's solution, the author has been enabled to detect choline in *flor. chamomill. vulg.*, *herb. millefolii*, *herb. meliloti.*, *fol. malvæ*, *herb. cochleariæ*, *fruct. anisi vulgaris*, *Cort. Sambuci*, and *Sem. robiniæ pseudacaciæ.* Bombelon's *bursine* has also proved to be nothing but choline. Choline, together with small quantities of betaine, have been found in the seeds of *Lathyrus sativus* and of *L. Cicera*. Tables are given showing the relative delicacy of the usual reagents for alkaloids towards different bases (betaine, choline) and towards different plant extracts (*Sem. arecæ*, *fol. millefolii*, &c.). J. J. S.

Homologues of Caffeine. By WILLEM VAN DER SLOOTEN (*Chem. Centr.*, 1896, i, 993—994; from *Diss. Marburg*, 1895, 1—45).—*Ethyltheobromine* (*homocaffeine*), which melts at 164—165°, and is not precipitated from its salts by ammonia, is prepared by heating the silver salt of theobromine with ethylic iodide, or, better, by the action of ethylic iodide on theobromine in presence of alcoholic potash. The aurochloride melts at 226°, the platinochloride above 240°. The author has described and analysed double compounds of ethyltheobromine with mercuric chloride, with mercuric cyanide, and with silver nitrate, and the hydrochloride, hydrobromide, sulphate, acetate, and oxalate. With methylic iodide, an additive product is formed which gives a platinochloride melting at 232°. Ethylic iodide does not form an additive product. Potassium hydroxide converts ethyltheobromine into *homocaffeidinecarboxylic acid*, whose copper salt,

$$(C_9H_{13}N_4O_3)_2Cu,4H_2O,$$

was analysed. By the action of bromine, a mono-substitution product melting at 171—172° is formed, and this, when treated with potassium hydroxide and alcohol, yields an ethoxy-compound, $OEt{\cdot}C_9H_{11}N_4O_2$, melting at 154°. Potassium dichromate and sulphuric acid oxidise ethyltheobromine to carbonic anhydride, methylamine, ammonia, and methylethylparabanic acid, which melts at 44°, and with potassium hydroxide decomposes into oxalic acid and methylethylcarbamide. By oxidation with nitric acid, ethyltheobromine yields methylamine methylethylparabanic acid and a compound melting at 137°. Potassium chlorate and hydrochloric acid at 50° convert ethyltheobromine into monochlorethyltheobromine, which melts at 111°, and a compound analogous to apocaffeine. The latter loses carbonic anhydride when boiled with water, and the solution so formed, on boiling with basic lead acetate, forms lead mesoxalate, a compound analogous to alloxan, but which cannot be reduced to amalic acid, being left in solution.

Propyltheobromine and *isobutyltheobromine* are prepared in a similar way to ethyltheobromine. The former melts at 136°, its platinochloride at above 240°, and its aurochloride at 93°; the latter melts at 129—130°, and its aurochloride at 97°. E. W. W.

Reaction between Herapathite and Barium Carbonate in Dilute Alcohol. By A. CHRISTENSEN (*Zeit. anorg. Chem.*, 1897, **14**, 297—301).—An alcoholic solution of herapathite containing iodine equivalent to 16·65 c.c. N/10 sodium thiosulphate solution, after treatment with barium carbonate, required only 13·55 c.c. of the thiosulphate. The difference in the quantity of iodine is due to a portion of the iodine being reduced by the alcohol whereby hydrogen iodide and acetic acid are formed; the sulphuric acid present was equivalent to 4·3 c.c. of a N/10 solution. For every 4 equivalents of iodine which are converted into hydrogen iodide, 5 equivalents of sulphuric acid are replaced or 5 equivalents of quinine saturated, although at the same time the solution remains neutral. This is effected by the oxidation of the alcohol to acetic acid and 4 atoms of iodine produce 1 molecule of this acid, and 4 molecules of hydriodic acid by which the quinine is saturated. E. C. R.

A Constituent of Cinchona Bark which gives the Reactions of "Digitalinum Verum." By A. BEITTER (*Arch. Pharm.*, 1897, **235**, 137—143).—It is shown that quininotannic acid gives the same reaction with sulphuric acid containing a ferric salt as has already been described by Kiliani (Abstr., 1896, ii, 551) as characteristic of "*digitalinum verum.*" It is therefore necessary, in testing for the latter, to be sure that cinchona bark or its constituents are absent. Extracts from different barks contain very unequal amounts of quininotannic acid, so that this acid not only occurs in different proportions in various barks but also probably occurs in numerous combinations. J. J. S.

Calcium Salt contained in Cinchona Bark and Preparation of Quinic Acid. By JOHAN E. DE VRIJ (*Chem. Centr.*, 1896, i, 937—938; from *Ned. Tydsch. Pharm.*, 1896, 70).—The calcium salt is extracted from the macerated bark, preferably *succirubra*, by cold water until the liquid no longer becomes turbid on heating with ammonium oxalate; exposure to air should be avoided. The extract is evaporated to a syrup in a vacuum and the salt precipitated by adding alcohol; the precipitate is then kneaded with alcohol, dissolved in water, and the cinchona-red which contaminates it removed by boiling the acid solution with magnesia. The author suggests that this plastic calcium salt is derived from an unknown compound formed by the union of quinic acid with quinotannic acid. Quinic acid is prepared from this salt by boiling its solution with a slight excess of calcium hydroxide and evaporating to dryness; during evaporation, the quinotannic acid is converted into cinchona-red, which remains with the lime and calcium quinate. The quinate is extracted with hot water, filtered, crystallised by evaporation, and the pure acid obtained from it by means of oxalic acid. E. W. W.

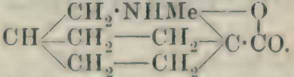
Strychnine Drugs. By G. SANDER (*Arch. Pharm.*, 1897, **235**, 133—137).—It is shown that the acid known as igasuric acid, which occurs in the officinal strychnine drugs (nux vomica and St. Ignatius' beans) is probably caffetannic acid, since on treatment with potash it yields glucose and dihydroxycinnamic acid (caffeic acid). Keller's method for estimating alkaloids in different drugs is strongly recommended as the best. The author suggests a method for estimating strychnine in the presence of brucine by destroying the brucine with potassium permanganate. The amount of strychnine in the mixed alkaloids from nux vomica varies from 43·9 to 45·6 per cent.; the latter number roughly corresponds with a mixture of strychnine and brucine in molecular proportion. In St. Ignatius' beans, the strychnine varies between 60·7 and 62·8 per cent., the higher number corresponding with 1 mol. of brucine to 2 mols. of strychnine. J. J. S.

Methylation of Hydrotropidine. By RICHARD WILLSTÄTTER *Ber.*, 1897, **30**, 721—728).—The methylation of hydrotropidine by A. W. Hofmann's method proceeds throughout normally, but somewhat differently from the methylation of tropidine. On treatment with freshly precipitated silver oxide and distillation, hydrotropidine methiodide yields *methylhydrotropidine* (dimethyl-Δ^3-tetrahydrobenzylamine), $C_7H_{11}\cdot NMe_2$, a liquid boiling at 189° (corr.), and giving the following salts, namely, a *platinochloride* separating from boiling water in orange-red prisms melting with decomposition at 192—193°; an *aurochloride* consisting of microscopic leaflets melting at 90°; a *methiodide* separating from absolute alcohol in slender needles melting and decomposing at 240°; and an *aurochloride* of the *methiodide* crystallising from dilute alcohol in short prisms melting with effervescence at 135°.

Hydrotropilidene, C_7H_{10}, is formed when an aqueous solution of methylhydrotropidine methiodide is treated with moist silver oxide, and the trimethylamine is removed by distilling the strongly alkaline solution of the methylhydrotropidinemethylammonium hydroxide formed; it is a colourless, highly refractive liquid boiling at 118—119° (120—121° corr.) under a pressure of 715 mm., its sp. gr. = 0·8929 at 0°. It yields an oily *hydrobromide* when treated with an acetic acid solution of hydrobromic acid. J. F. T.

Dihydroecgonidine. By RICHARD WILLSTÄTTER (*Ber.*, 1897, **30**, 702—721).—On reduction with sodium in amylic alcohol solution, anhydroecgonine, or its ethylic salt, passes quantitatively into a saturated compound of the empirical formula $C_9H_{15}NO_2$, for which the author proposes the name dihydroecgonidine.

Dihydroecgonidine is a crystalline compound of neutral reaction closely resembling anhydroecgonine, but somewhat more stable; it gives well-defined crystalline salts with mineral acids. Its ethylic salts are liquids, not decomposed by distillation under diminished pressure. It is inactive, the two asymmetric carbon atoms of anhydroecgonidine having become symmetrical by the saturation of the hydrobenzene ring. From the Merling-Einhorn formula for anhydroecgonine, it must possess the constitution



When dried in a vacuum over sulphuric acid, dihydroecgonidine contains $\frac{1}{2}H_2O$; this it loses at 105°, and then melts at 200°. The *hydrochloride* crystallises in glistening transparent plates melting at 234—236°, the *platinochloride* in orange-yellow prisms containing $2H_2O$, and the *aurochloride* in yellow scales containing $3H_2O$ and decomposing at 210—212°. The *ethylic* *salt of dihydroecgonidine* is a colourless liquid boiling at 137—139° (corr.) at 20 mm., and differing from the ethylic salt of anhydroecgonidine in giving a precipitate with picric acid in concentrated solutions only; the *aurochloride* of this ethylic salt crystallises in glistening, yellow prisms melting at 121—122°, and the *methiodide* in long needles melting at 156°. The *aurochloride* of ethylic dihydroecgonidine methochloride separates from dilute alcohol in scales melting at 168—169°, and the *aurochloride* of dihydroecgonidine from water as a canary-yellow powder containing $4H_2O$, or from concentrated hydrochloric acid as microscopic prisms melting and decomposing at 255°.

Ethylic methyldihydroecgonidine, $NMe\cdot C_7H_{10}\cdot COOEt$, is best prepared by treating a hot aqueous solution of the methiodide with potassium carbonate; it is a colourless oil boiling at 156° (corr.) under a pressure of 16 mm., and having a strongly alkaline reaction; the *platinochloride* separates from hot water in orange-red, or from alcohol in pale yellow scales melting at 148°. The *methiodide* crystallises from absolute alcohol in flat plates melting at 149—150°, whilst the *aurochloride* of the *methochloride*, obtained by the action of silver chloride and gold chloride on the above, forms small, glistening prisms melting at 153—154°.

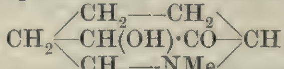
Dihydrotropilidenecarboxylic acid, $C_7H_9\cdot COOH$, is obtained on treating the methiodide of ethylic methyldihydroecgonidine with caustic soda at 120°; it crystallises from hot alcohol in long, glistening needles melting at 74—75°, and is volatile with steam; the *silver* salt crystallises from water in small needles, and the *tetrabromide* from concentrated formic acid in colourless, glistening scales melting with decomposition at 196—197°. J. F. T.

Arecoline Methiodide. By RICHARD WILLSTÄTTER (*Ber.*, 1897, **30**, 729—730).—The reaction between arecoline and methylic iodide is very violent, and it is necessary to dilute the base with methylic alcohol before adding the iodide.

Arecoline methiodide is a colourless solid, crystallising from absolute alcohol in glistening prisms, and melting at 173—174°; it yields an *aurochloride* which crystallises from methylic alcohol in golden-yellow, rhombic leaflets melting at 134—135°. On fusion with potash, it splits up into dimethylamine and a fatty acid.

Dihydroarecoline methiodide crystallises in nodular masses melting at 155—156°, and the *aurochloride* of the methochloride in glistening flakes melting at 111—112°. J. F. T.

"Scopolaminum Hydrobromicum" and Scopoline. By ERNST SCHMIDT (*Chem. Centr.*, 1896, i, 1199—1200; from *Apoth.-Zeit.*, **11**, 260—262).—According to Hesse (Abstr., 1896, i, 655, and 1897, i, 132), commercial scopolamine hydrobromide consists of a mixture of the hydrobromides of hyoscine and atroscine. The author was unable, however, to isolate either of these bases from the root of *Scopolia* or the seed of *Hyoscyamus*, but obtained scopolamine in considerable quantity (Abstr., 1896, i, 712). Samples of the commercial scopolamine hydrobromide (Merck, Gehe) showed a very varying specific rotatory power ($[\alpha]_D = -25\cdot43°, -14\cdot58°, -17\cdot9°, -6\cdot62°$, &c., although identical in other properties. From a strongly lævorotatory aqueous solution, a nearly inactive scopolamine was obtained by the action of silver oxide. Moreover, from the same *Scopolia* root a hydrobromide of normal and one of very slight rotatory power were isolated, hence the various rotatory powers of the ordinary hydrobromide must be ascribed to the presence of an inactive scopolamine which does not exist in the root, but is formed during the extraction. In respect to physiological action, according to Uhthoff and Axenfeld, there is no difference between the hydrobromides of strong and weak rotatory power. Scopoline, $C_8H_{13}NO_2$, obtained from scopolamine, forms a *monoacetyl* derivative, and with hydriodic acid and amorphous phosphorus yields, in addition to ammonia, methylamine and a hydrocarbon, a hydriodide of a *base*, $C_8H_{15}N$, which is isomeric with hydrotropidine, and very similar to it. Scopoline is scarcely acted on by potassium dichromate and sulphuric acid, but, like tropine, is attacked by barium permanganate, and forms *scopoligenine*, $C_7H_{11}O_2N$, which melts at 205—206°, and gives a *nitroso*-compound, melting at 174—175°. With methylic iodide, scopoligenine re-forms scopoline, which must therefore contain the group NMe. A *methiodide*, $C_8H_{13}NO_2,MeI$, can also be prepared, and this forms an ammonium base which, on distillation, yields *methylscopoline*, $C_8H_{12}MeNO_2$, a compound very similar to methyltropine and boiling at 244°. Methylscopoline unites with methylic iodide to form *methylscopoline methiodide*, $C_8H_{12}MeNO_2,MeI$, and this, on distillation with potassium hydroxide, gives trimethylamine and an unstable substance, $C_7H_8O_2$.

All these reactions of scopoline are in accordance with a composition represented by a formula,  $CH_2\left\langle\begin{array}{l}CH_2\text{---}CH_2\\ CH(OH)\cdot CO\\ CH_2\text{---}NMe\end{array}\right\rangle CH$; this is analogous to Merling's tropine formula, and has been already ascribed to scopoline by Eijkman from measurements of the refractive index.

E. W. W.

Douradinha, or Leaves of Palicourea rigida. By KARL G. SANTESSON (*Arch. Pharm.*, 1897, **235**, 143—150).—The author has obtained a small quantity of an alkaloidal substance from douradinha. It crystallises from its alcoholic solution in colourless needles, or in small prisms and cubes, practically insoluble in water, but readily soluble in alcohol and ether, yielding alkaline solutions. The dried substance sinters at 226—230°, and melts at 235°. With potassium dichromate and concentrated sulphuric acid, the base is coloured yellowish-red, changing rapidly to purple, then to blue-red, and finally to mahogany-brown; vanadin-sulphuric acid causes a deep red coloration, which changes from brown to green. The usual reagents for alkaloids give copious precipitates. A crystalline *sulphate* and a similar *nitrate* have been obtained. The physiological action of the alkaloid on frogs has been studied; it has slight poisonous properties, and causes paralysis of the central nervous system. J. J. S.

Compound of Albumin with Phenol. By M. SHIMADA (*Bull. Coll. Agric. Imp. Univ. Tokyo*, 1897, **2**, 507—509).—*Triphenylalbumin*, $C_{72}H_{109}Ph_3N_{18}SO_{22}$, is formed when finely powdered egg-albumin is heated for some hours on a water bath with phenol (10 parts); it is precipitated as a flocculent mass by alcohol, and washed with alcohol and water. The compound has no odour or taste, is insoluble in boiling alcohol and water and in aqueous potassium carbonate, readily soluble in hot phenol, and dissolves in 0·5 per cent. caustic potash solution, from which it is precipitated by acetic acid; in strong acetic acid, the substance gradually swells up. It is not attacked by cold hydrochloric acid containing 10 per cent. HCl or by 5 per cent. nitric acid, but 35 per cent. hydrochloric acid gradually dissolves it. The compound gives the biuret and Millon's reaction like ordinary albumin.

Prolonged digestion at 100° with strong hydrochloric acid did not liberate phenol from the compound, and the same negative result, as regards phenol, was obtained after digestion with 30 per cent. sulphuric acid (first at 100° and afterwards on a sand bath). In this experiment, leucine and tyrosine were produced, but the amount of substance was insufficient to decide whether argenine, lysine, and aspartic, glutamic, and phenylamidopropionic acids were formed.

Triphenylalbumin is a good nutrient for micro-organisms, and, like ordinary albumin, is subject to fermentation. N. H. J. M.

Chemical and Physiological Reactions of certain Synthesised Proteid-like Substances. By JOHN W. PICKERING (*Proc. Roy. Soc.*, 1897, **60**, 337—349).—The author has prepared a series of colloidal substances from certain derivatives of proteids and other substances.

Fractional heat coagulation shows them to be mixtures of different substances which exhibit different physiological actions. When introduced into the circulation of pigmented rabbits, dogs, or cats, intravascular coagulation of the blood is produced in a similar manner to that with a nucleoproteid. They hasten the coagulation of the blood withdrawn from the carotid, and will, when slowly injected intravenously in minute quantities in dogs, produce a retardation of the coagulability of the intravascular blood.

Colloid a is obtained as a pinkish-grey, friable powder, when equal parts of metamidobenzoic acid and biuret are heated with three times their weight of phosphoric anhydride in a sealed tube at 125°. It dissolves in ammonia, from which, on gentle evaporation, translucent, yellowish plates are obtained readily soluble in warm water. The aqueous solution is neutral, lævorotatory ($a_D = -52$), and does not coagulate on heating; but if a trace of a soluble salt of barium, strontium, calcium, magnesium, or sodium is added, a pronounced coagulum is obtained.

The precipitate formed on the addition of lead acetate resembles a similar precipitate obtained from a proteid solution, in redissolving when hydrogen sulphide is passed through the solution in which it is suspended. The chemical nature of the substance is apparently unchanged, but physiologically its behaviour is quite different, as when injected intravenously into pigmented rabbits or dogs, it does not induce intravascular coagulation.

Colloid β is produced when equal weights of tyrosin, biuret, and twice the weight of phosphorus pentachloride are heated in sealed tubes for 6 hours at from 125—130°. It is a grey powder, insoluble in cold water, and only sparingly soluble on warming; it dissolves readily in concentrated aqueous ammonia, giving an opalescent lævorotatory solution ($\alpha_D = -48$).

Colloid γ is a sparingly soluble white powder, obtained by heating together in sealed tubes at 130° a mixture of equal weights of alloxan and metamidobenzoic acid with twice their weight of phosphoric anhydride. It dissolves in ammonia, forming an opalescent, straw-coloured solution, which, on evaporation, yields translucent plates; the latter are soluble in water, forming a straw-coloured, opalescent lævorotatory solution ($\alpha_D = -41$). It does not produce intravascular coagulation when intravenously injected into pigmented rabbits, nor does it retard coagulation of blood withdrawn from the carotid.

Colloid δ is formed when equal weights of paramidobenzoic acid and phosphorus pentachloride are heated in sealed tubes at 125° for 3 hours; it is a grey, friable powder insoluble in cold water. From its ammoniacal solution, it is obtained as translucent yellow plates, which dissolve in warm water, forming a straw-coloured, opalescent solution which is lævorotatory ($\alpha_D = -42$).

Colloid ϵ is produced when equal weights of tyrosine and xanthine, and twice their weight of phosphorus pentachloride, are heated in sealed tubes at 125°. It is a yellowish powder, slightly soluble in warm water, and readily in concentrated ammonia; from this solution, on gentle evaporation, it is obtained as translucent, yellow plates, similar to those already described. Its aqueous solution is lævorotatory ($\alpha_D = -38$).

Colloid ζ is prepared in a similar manner to colloid ϵ, hypoxanthine being substituted for xanthine. It resembles the colloid ϵ in all respects, and has a rotatory power of $\alpha_D = -40$.

Colloid η, obtained by the interaction of tyrosine and phosphorus pentachloride, is a pink, friable powder, sparingly soluble in both cold and warm water, but readily in aqueous ammonia. It does not yield any of the distinctive colour reactions of the proteids, and fails to produce intravascular coagulation when intravenously injected into rabbits.

Experiments on the fractional heat coagulation of these synthesised colloids are also described. A. W. C.

Proteose of Wheat. By Thomas B. Osborne (*Amer. Chem. J.*, 1897, 19, 236—237).—A reply to G. E. Teller (this vol., i, 304).

Organic Chemistry.

Butanes and Octanes in American Petroleum. By CHARLES F. MABERY and EDWARD J. HUDSON (*Amer. Chem. J.*, 1897, **19**, 243—262).—After very careful examination of the lowest fractions obtained from Pennsylvania and Ohio petroleum, the authors conclude that it contains only one butane, namely, isobutane, which is shown by the boiling points of its chloro-derivative, 67—68°, of the corresponding alcohol, 108—109°, and of the sulphide, 172°. This is contrary to what has hitherto been assumed, namely, that the butane is the normal hydrocarbon.

The isobutane is contained principally in the fraction boiling between −2° and 2°. The chief product of chlorination is the monochloro-derivative (boiling point 67—68°); but, by repeated fractionation, a small amount of a substance distilling fairly constantly at 121—122° was also obtained. This proved to be a dichlorobutane mixed with the monochloro-derivative, but the former was not present in sufficient quantities for complete examination.

Monochloro- and a small amount of a dichloro-pentane were prepared from the fraction of petroleum boiling between 29—30°.

For the examination of the octanes, a portion of Ohio petroleum boiling between 75° and 160° was examined. The octanes were separated exceedingly slowly by fractional distillation, and it was not until after thirty-seven distillations that a large fraction boiling between 118·5—119·5° was obtained. This proved to be an octane yielding a monochloro-derivative boiling at 164—166°.

In addition to this, a second octane was obtained which boiled at 124—125°, and gave a chloro-derivative boiling at 173—174°. Ohio petroleum does not contain an octane with a higher boiling point than 125°, nor any of the following hydrocarbons which have been isolated by various investigators from similar fractions of other petroleums, namely, hexahydromesitylene, di-isobutyl, and isoctonaphthene.

A. W. C.

Di-iodacetylene and Tetriodethylene. By HEINRICH BILTZ [with STEPHAN WERNER] (*Ber.*, 1897, **30**, 1200—1210).—A mixture of di-iodacetylene and tetriodethylene is formed by the action of iodine dissolved in potassium iodide solution on calcium carbide, the product being free from di-iodethylene. This substance was described by Maquenne (Abstr., 1893, i, 449) as di-iodacetylene, a similar mixture having also been obtained by Berend (*Annalen*, 1865, **135**, 257). Pure di-iodacetylene is obtained by distilling this mixture with water vapour at 100 mm. pressure, or with acetic acid, the pure substance passing over into the distillate. It crystallises in small, colourless, brittle needles melting at 78°, has a repulsive odour and volatilises very readily, its vapour attacking the mucous membrane violently.

Tetriodethylene has previously been described by Maquenne and

Taine (*Apoth. Zeitung*, 1893, **8**, 613). It is non-volatile and odourless and melts at 187°.

Di-iodacetylene yields tetriodethylene when it is dissolved in water and heated at 100° (Meyer and Pemsel, Abstr., 1896, i, 517), when it is exposed to light, or when it is dissolved in alcohol and concentrated sulphuric acid added to the solution.

Both di-iodacetylene and tetriodethylene are converted by chlorine into hexachlorethane, and by bromine into hexabromethane.

When di-iodacetylene is treated in ethereal solution with nitrous fumes (from nitric acid and arsenious oxide), it yields *nitrotri-iodethylene*, $CI_2{:}CI\cdot NO_2$, which crystallises in lemon-yellow, silky needles, and melts at 107°. A better yield is obtained when an ethereal solution of iodine is added. The compound is not decomposed when heated with alcoholic potash or alcoholic sulphuric acid.

An unstable substance, which was probably an impure form of this compound, was described by Berend (*loc. cit.*). A. H.

Sodium Carbide and Monosodacetylene. By CAMILLE MATIGNON. (*Compt. rend.*, 1897, **124**, 775—777).—Between its melting point and 190°, sodium decomposes acetylene with production of monosodacetylene, C_2HNa. Above 210°, sodium carbide, C_2Na_2, is formed, whilst beyond 210—220°, monosodacetylene decomposes into acetylene and sodium carbide, and at the same temperatures sodium acts on monosodacetylene, with liberation of hydrogen and formation of sodium carbide. All these reactions are quantitative, and the products are white solids. It is, however, essential to constantly agitate the sodium in order to prevent too great local rises of temperature with consequent separation of carbon. The sodium is best contained in a flask which is heated in an oil bath, and the acetylene must be carefully dried. C. H. B.

Ammonium Cyanide and its Manufacture. By DENIS LANCE (*Compt. rend.*, 1897, **124**, 819—821).—When ammonia is passed slowly over wood charcoal heated at 1000—1100°, ammonium cyanide is always formed, contrary to the statement of Bueb and Bergmann. The yield of cyanide is at a maximum at this temperature, and 25 per cent. of the nitrogen in the ammonia is converted into cyanogen. This yield is, however, greatly increased if the ammonia is mixed with nitrogen and hydrogen, especially when the latter is in excess, and the yield of cyanogen may be nearly 90 per cent. of the ammonia when 200 c.c. of ammonia is mixed with 5000 c.c. of hydrogen and 500 c.c. of nitrogen. Under these latter conditions, at least 70 per cent. of the nitrogen in the ammonium cyanide is derived from the free nitrogen in the gaseous mixture. C. H. B.

Hydrocobaltocobalticyanic Acid and its Salts. By C. LORING JACKSON and ARTHUR M. COMEY (*Amer. Chem. J.*, 1897, **19**, 271—281). —When potassium cobalticyanide is boiled with strong nitric acid, the mixture gradually turns red, the colour increasing with prolonged boiling, and after a time the whole is converted into a semi-solid, gelatinous mass. The product is purified by heating with nitric acid and then washing with water; the insoluble jelly thus obtained is dried in a vacuum, when it changes in colour from red to a greyish green. It is very hygroscopic, absorbing water from the air rapidly and regaining its red colour. Analysis shows that the substance has the composition $KH_2Co_3(CN)_{11}H_2O$; and it is, therefore, *monopotassium cobaltocobalticyanide.* The crude product is insoluble in cold water, and nearly so in hot water, but after the impurities are washed out it dissolves slowly. The solution has a strong acid reaction, and gives precipitates with salts of many of the heavy metals.

When a solution of the monopotassium compound is treated with excess of potash, it turns dark brown, and, on boiling, a black precipitate of cobaltic hydrate is thrown down. If the boiling is continued until no more precipitation takes place, the liquid filtered, and the light yellow filtrate acidified with acetic acid and precipitated with alcohol, white needles are obtained, which prove to be potassium cobalticyanide. This salt generally crystallises in broad, rhombic crystals, the form in which it here appears being due, in all probability, to a small amount of impurity.

The *dipotassium*, *barium*, *silver*, *copper*, and *zinc* salts of cobaltocobalticyanic acid are also described. A. W. C.

Action of Mercuric Chloride on Alcohols. By FONZES-DIACON (*Bull. Soc. Chim.*, 1897, [iii], 15, 762—763).—Alcohols are oxidised when boiled with mercuric chloride, with formation of aldehydes and precipitation of mercurous chloride. In the case of a solution of mannitol, the reaction was found to be particularly rapid.

M. W. T.

Constitution of Phosphorous Acid. By C. A. AUGUST MICHAELIS and THEODOR BECKER (*Ber.*, 1897, **30**, 1003—1009).—The constitution of phosphorous acid (*Annalen*, 1876, **181**, 312) has not hitherto been definitely settled, since the various reactions in which it takes part can all be interpreted, both by the symmetric formula, $P(OH)_3$, and the asymmetric formula, $PHO(OH)_2$. The author has now succeeded in obtaining further evidence in favour of the latter of these.

When lead phosphite, $PbHPO_3$, is treated with ethylic iodide at 175°, it yields the diethylic phosphite, $PHO(OEt)_2$, which was obtained by Thorpe and North by the action of phosphorous anhydride on alcohol (Trans., 1890, 634). When this compound is treated in ethereal solution with sodium, and then with ethylic iodide, it yields *diethylic ethylphosphinite*, $PEtO(OEt)_2$, which is isomeric with ethylic phosphite, $P(OEt)_3$, and differs from it in all its properties. Thus, it boils at 198°, has a sp. gr. = 1·025 at 21°, and in aqueous solution does not reduce mercuric chloride or precipitate magnesium mixture, whereas ethylic phosphite reduces mercuric chloride, boils at 191°, and has a sp. gr. = 1·075.

Diethylic ethylphosphinite is also formed when *ethyloxychlorophosphine*, $PEtOCl_2$, which is prepared by the action of sulphurous anhydride on ethylchlorophosphine, and boils at 175—178°, is treated with sodium ethoxide.

Ethylphosphinous acid, therefore, stands in the same relation to phosphorous acid as ethylsulphonic acid to sulphurous acid. A. H.

Molecular Modifications and Multirotation of the Sugars. By CHARLES TANRET (*Bull. Soc. Chim.*, 1896, [iii], **15**, 195—205, and

349—361).—The author has shown that, in the case of glucose and in that of isodulcitol (Abstr., 1895, i, 490; 1896, i, 334), the multirotation of the sugar solutions is due to a transformation of one modification into another under the influence of water. *Galactose*, like glucose, exists in three modifications. The ordinary or α-galactose, when freshly dissolved in water, has a rotatory power $[\alpha]_D = +135°$. The rotatory power diminishes when the solution is left to itself, or more rapidly when the solution is boiled, and at length attains a value of $[\alpha]_D = +81·6°$. The galactose is then completely converted into the β modification. But if galactose is dissolved in hot alcohol, its rotatory power is reduced eventually to $[\alpha]_D = +53°$, and it is converted into a new or γ modification. Both the β and γ modifications can be obtained in solid condition by crystallisation from mixtures of alcohol and water. *Arabinose* forms two modifications. When first dissolved in water, the ordinary or α form has a value $[\alpha]_D = +175°$. This changes, however, gradually, and falls to $[\alpha]_D = +104—105°$. The α has then been converted into the β modification. β-Arabinose can be obtained by precipitating arabinose from its cold aqueous solutions by means of alcohol. *Xylose* behaves like arabinose, the rotatory power in aqueous solution falling from $[\alpha]_D = +78°$ to $[\alpha]_D = +18·9°$. Pure crystals of β-xylose could not be obtained. *Milk-sugar*, like glucose and galactose, exists in three modifications. The α form has the rotation $[\alpha]_D = +92·6°$, and crystallises out from cold, aqueous solutions of milk-sugar. The β modification, $[\alpha]_D = +56°$, is formed when the crystallisation takes place at 85—86°. The γ form is produced by precipitating milk-sugar from the aqueous solutions with alcohol. Its rotation is $[\alpha]_D' = +34·5°$.

Each modification of a sugar has then its own rotatory power, and it appears, therefore, that the multirotation of the reducing sugars is due to the transformation of one modification into another in aqueous solution. H. C.

Chemistry of Honey. By O. KÜNNMANN and ALBERT HILGER (*Chem. Centr.*, 1896, ii, 476—478; from *Forsch.-Ber. Lebensm. u. Bez. Hygiene*, &c., 3, 211—226).—Lævorotatory honeys contain only traces of dextrins, whilst in all dextrorotatory forest honeys they are present in greater quantity and bear a direct relation to the rotatory power. Hence honeys of the former class, on fermentation with large amounts of yeast, easily produce an inactive residue after fermentation. Von Raumer and Mader have shown that pressed yeast acts more strongly on honey dextrin than beer-yeast, hence Sieben, who always used the former, invariably obtained inactive residues from pure honeys, and regarded honeys which yielded dextrorotatory residues as adulterated. In order to obtain an exact comparison of the powers of fermentation of the various yeasts, the authors experimented with a dextrin which had been carefully isolated from dextrorotatory honey. Solutions were prepared containing the other necessary components of honey in their natural proportions. Fermentation was carried on at 25° for 140 hours in flasks charged with 150 c.c. of solution, with 10 grams of yeast, and closed by cotton-wool plugs. Three beer yeasts from different breweries, freed from wort by water, yielded slightly dextrorotatory residues. Two pressed yeasts from different sources produced inactive residues. Pressed yeasts always contain schizomycetes. A species of yeast obtained from pressed yeasts by pure cultivation and free from schizomycetes gave a far less energetic fermentation and left a dextrorotatory residue. Wine yeasts were incapable of fermenting honey-dextrin; in 16 to 20 days, only 8·7 to 13·1 per cent. of dextrin was attacked. Beer yeasts worked more actively, but the *Saccharomyces Pombe* from Africa was the only one which effected complete fermentation; in other cases, only from about 25 to 40 per cent. was fermented. The last portions of invert-sugar are only attacked after prolonged fermentation. In many cases, after employing the osazone test, a flocculent, yellow mass separated from the cooled filtrate from the glucosazone, but its quantity was insufficient to allow of examination.

Larger quantities of honey-dextrin were obtained by repeated precipitation by alcohol, and removal of diffusable substances by dialysis, &c., the liquid being finally treated with ether and alcohol, and the precipitate dried. It forms a snow-white, almost tasteless, amorphous powder, easily soluble in water, contains 0·3 to 0·5 per cent. of ash, and is far less hygroscopic than the product obtained before dialysing. Its aqueous solution is neutral, reduces Fehling's solution on boiling; the filtrate after inversion of the sugar by hydrochloric acid is again capable of reducing Fehling's solution, and possesses a rotatory power of about half its original value. Large quantities of glucosazone were obtained by means of phenylhydrazine from the neutralised inverted solution. A dilute solution of iodine in potassium iodide does not produce a coloration, hence achroodextrin with only the slightest traces of erythrodextrin can be present, and none of the latter could be obtained by fractionation with 75 per cent. alcohol. As a preliminary proof of the presence of a disaccharide, the phenylhydrazine test was employed and an osazone melting at 145—147° and evolving gas at 178° was obtained. Isomaltosazone melts at 153—155°. As Ost, Brown and Morris and Jalowetz have shown, however, that phenylhydrazine in presence of dextrin does not give a pure maltosazone, the authors repeated Ost's experiments and found that a variety of osazones melting between 145° and 175° were obtained by varying the proportions of dextrin and maltose. The honey-dextrin was, therefore, treated by Lintner and Düll's method, namely, fractionating a 20 per cent. solution with 90 per cent. alcohol, and then with 85 per cent. alcohol, until the reducing power was 18 (maltose = 100). Finally, fractionation of a 10 per cent. solution with 80 per cent. alcohol was carried on until phenylhydrazine gave no osazone, and the product then dialysed until it was free from ash. The solution remaining on the membrane was evaporated in a vacuum, dissolved in 2 parts of water, and precipitated by alcohol and ether. On reprecipitating from a 10 per cent. solution by 80 per cent. alcohol, both precipitate and filtrate showed the same specific rotatory power $[\alpha]_D = +191°$, and a reducing power = 10. Hence this dextrin is identical with Lintner's achroodextrin obtained by means of diastase, and with Mittelmeier's achroodextrin isolated from beer wort. It could not be obtained in a crystalline form, but its molecular weight, as determined by the freezing point method, was 1926, which corresponds approximately with the formula $(C_{10}H_{20}O_{10})_6 + H_2O$.

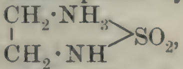
All the fractions obtained in the preparation of the dextrin possessing a rotatory power of less than 145° were mixed and evaporated in a vacuum. Finally, by mixing all the solutions of a rotatory power of from about $+140°$ to $+145°$ and precipitating from a 20 per cent. solution by 90 per cent. alcohol, a substance of rotatory power $= +140{\cdot}8°$ was obtained. By precipitating from a 30 per cent. solution in methylic alcohol by gradual addition of absolute alcohol, its rotatory power was reduced to 140°, and after dialysing three times, allowing four-fifths of the solution to pass through the membrane, the rotatory power of the residue was $+159°$, and that of the solution which had passed through 139°. From the latter, a light yellow osazone, crystallising in small needle clusters, was obtained. After drying over sulphuric acid, it had a specific rotatory power $[\alpha]_D = +54°$, and after drying at 100°, melted at 184—186°. This disaccharide is probably maltose, although maltosazone has a specific rotatory power $[\alpha]_D = +61°$, and melts at 202—206°.

In the separation of achroodextrin from dextrorotatory honey by dialysis, it was found that, by prolonging the process, an achroodextrin containing maltose remained on the membrane ($[\alpha]_D = +187{\cdot}5°$, reducing power $= 15{\cdot}9$), and the solution outside the membrane ($[\alpha]_D = +161°$) contained small quantities of achroodextrin.

E. W. W.

Preparation of Primary Amines. By MARCEL DELÉPINE (*Compt. rend.*, 1897, **124**, 292—295).—In a previous communication (Abstr., 1895, i, 326), the author has shown that when hexamethylenetetramine alkyliodides are boiled with dilute hydrochloric acid, they are hydrolysed in accordance with the equation $C_6H_{12}N_4RI + 6H_2O = 6CH_2O + 3NH_3 + NRH_3I$. In alcoholic solution, these reactions occur more readily, owing partly to the development of energy due to the formation of methylene diethoxide by the interaction of the formaldehyde with the alcohol. The equation then becomes $C_6H_{12}N_4RR' + 3HCl + 12C_2H_6O = 6CH_2(OEt)_2 + 3NH_4Cl + NRH_2HR'$, R representing the alkyl group and R′ the halogen. For the preparation of allylamine, one molecular proportion of allylic iodide is added to a mixture of hexamethylene tetramine with four times its weight of chloroform. On warming, the reaction proceeds rapidly. The crystalline double salt, $C_6H_{12}N_4{\cdot}C_3H_5I$, is separated and dissolved in a mixture of 95 per cent. alcohol and aqueous hydrochloric acid (sp. gr. 1·33) in the proportions demanded by the above general equation. On gently warming, the reaction occurs and the liquid separates into two layers, the upper one consisting of methylene diethoxide, the lower one containing the ammonium chloride and the salt of the amine partly in solution and partly in the solid state. The methylene diethoxide is distilled off, and the residue twice treated with a further quantity of alcohol and acid, in order to decompose the intermediate methylenic compound of the amine which is formed. After distillation and treatment of the residue with a caustic alkali, the amine is easily obtained. By substituting benzylic chloride for the allylic iodide in the above preparation, benzylamine is readily prepared, 70 grams of hexamethylenetetramine and 70 grams of benzylic chloride yielding 45 grams of the pure amine. A. C. C.

Preparation of Allylamine. By SIEGMUND GABRIEL and GEORG ESCHENBACH (*Ber.*, 1897, **30**, 1124—1125).—The authors recommend the use of hydrochloric acid instead of sulphuric in Hofmann's method for the preparation of allylamine (*Ber.*, 1868, **1**, 183). Allythiocarbimide (50 grams) is boiled with 20 per cent. hydrochloric acid (200 c.c.) until the oil is completely dissolved, an operation which requires some 5 hours. The mixture is evaporated on the water bath, the crystalline mass dissolved in as little water as possible, then decomposed with caustic potash, and the oily base separated. The yield is about 76 per cent. of the theoretical. J. J. S.

Thionyl Derivatives of the Aliphatic Diamines. By C. A. AUGUST MICHAELIS and PAUL GRAENTZ (*Ber.*, 1897, **30**, 1009—1014. Compare Abstr., 1893, i, 504).—Ethylenediamine reacts with thionyl chloride to form *dithionylethylenediamine*, $SO{:}N{\cdot}CH_2{\cdot}CH_2{\cdot}N{:}SO$, which is a pale yellow, viscid liquid of characteristic penetrating odour, solidifies at 5·5° and boils at 100° (pressure = 25 mm.); it decomposes gradually when preserved, and is also readily decomposed by water. Ethylenediamine also reacts with thionylaniline to form an unstable yellow product. When ethylenediamine is suspended in ether and treated with sulphurous anhydride, an unstable compound is formed which passes by loss of sulphurous anhydride into the *compound*,  $\left.\begin{array}{l}CH_2{\cdot}NH_3\\ |\\ CH_2{\cdot}NH\end{array}\right>SO_2$, which is probably an internal salt of ethylenethionamic acid, and is a white, very hygroscopic mass, which decomposes when heated. More stable products are formed by the action of aldehydes on the ethylenethionamic acid. When benzaldehyde is added to an alcoholic solution of ethylenediamine saturated with sulphurous anhydride, *benzaldehyde-ethylenethionamic acid*,

$$NH_2{\cdot}C_2H_4{\cdot}N(SO_2H){\cdot}CHPh{\cdot}OH,$$

is formed, which crystallises in small, white plates and melts at 169°. *Salicylaldehyde-ethylenethionamic acid* is a pale yellow, hygroscopic, crystalline powder, which decomposes when heated.

Anisaldehyde-ethylenethionamic acid forms small, white needles melting at 166°. The *cinnamaldehyde* compound melts and decomposes at 165°. Furfuraldehyde also yields a *compound*, which forms stellate aggregates of brown needles, melting at 153°.

Dithionyltrimethylenediamine, $SO{:}N{\cdot}CH_2{\cdot}CH_2{\cdot}CH_2{\cdot}N{:}SO$, is a golden-yellow liquid which boils at 117° (pressure = 26 mm.). *Benzaldehyde-trimethylenethionamic acid* melts at 102°; the *salicylaldehyde* compound is a lemon-yellow, hygroscopic powder, melting at 104°; the *anisaldehyde*, *cinnamaldehyde*, and *furfuraldehyde* compounds are all hygroscopic and decompose on melting. A. H.

Action of Ethers on Phosphonium Iodide. By PETER FIREMAN (*Ber.*, 1897, **30**, 1088—1090).—Methylic and ethylic ether react with phosphonium iodide in the same manner as the corresponding alcohols, the tertiary base and quaternary iodide being produced, but no primary or secondary base being formed. The reaction, however, proceeds at a lower temperature when the ethers are employed, probably on account of the fact that only half as much water is produced in the reaction with the ethers as in that with the alcohols. A. H.

Condensation-products of Isovaleraldehyde. II. By LEOPOLD KOHN (*Monatsh.*, 1897, 18, 189—198. Compare Abstr., 1896, i, 10, 461).—When isovaleraldehyde is mixed with a very little solid potassium hydroxide, the mixture at once cooled and kept cool until the reaction is over, the product treated with water, saturated with carbonic anhydride, and the oil washed with water, a quantitative conversion of isovaleraldehyde into *isovaleraldol*,

$$CH_2Pr^{\beta}\cdot CH(OH)\cdot CHPr^{\beta}\cdot CHO,$$

is realised. This substance boils at 120° under 18 mm. pressure; it can sometimes be distilled unchanged, but at other times it will decompose into isovaleraldehyde. When distilled under atmospheric pressure, it loses water and yields an unsaturated aldehyde, *isopropylisobutylacraldehyde*, $CH_2Pr^{\beta}\cdot CH\colon CPr^{\beta}\cdot CHO$, and the same reaction occurs when an attempt is made to prepare an acetyl derivative, or to reduce it to a glycol. It can, however, be oxidised with potassium permanganate to an *acid*, $CH_2Pr^{\beta}\cdot CH(OH)\cdot CHPr^{\beta}\cdot COOH$, which melts at 56°, but has a great tendency to form a syrup which crystallises with difficulty; the acid, melting at 120°, to which Wohlbruck (Abstr., 1888, 1099) assigned the same constitution, must be differently constituted. By the action of hydroxylamine on the aldol, the *oxime* was obtained, together with those of valeral and of the acraldehyde; it boils at 169° under 25 mm. pressure, but it tends to lose water when distilled, or when treated with acetic anhydride; in the first case, the oxime of the acraldehyde is formed, in the second, the nitrile of the acid $C_{10}H_{18}O_2$.
C. F. B.

Fatty Ketones of High Molecular Weight. By JOSEPH BERTRAND (*Bull. Soc. Chim.*, 1897, [iii], 15, 764—768).—*Ethyl pentadecyl ketone* is formed by the action of palmitic chloride on zinc ethyl in ethereal solution, and subsequent treatment of the product with water; it is a white, crystalline substance which melts at 53°, boils at 197·5° under 11 mm. pressure, and is soluble in alcohol, ether, and light petroleum, but insoluble in water. Immediately after distillation, it melts at 50·5°, but after a time the substance undergoes some physical change, and its melting point rises to 53°. *Propyl pentadecyl ketone*, obtained by the action of palmitic chloride on zinc propyl in ethereal solution, is a white substance which immediately after distillation melts at 48°, but after some time at 50·5°; it distils without much decomposition at 211° under 11 mm. pressure, is insoluble in water, but soluble in alcohol, ether, and light petroleum, and when oxidised with chromic acid mixture, yields pentadecoic acid, melting at 51°. Both these ketones give oximes with hydroxylamine hydrochloride, and unstable hydrazones with phenylhydrazine. *Ethyl pentadecyl ketoxime* is a white solid, soluble in alcohol and ether, but insoluble in water; it softens at 42°, melts at 44°, and boils without decomposition. *Propyl pentadecyl ketoxime* melts at 28°. M. W. T.

Conversion of Oleic Acid into Stearolactone and Hydroxystearic Acid. By DAVID (*Compt. rend.* 1897, 124, 466—468).—If ice-cold water is added to a mixture of oleic acid and monhydrated sulphuric acid in molecular proportion, care being taken to avoid any rise of temperature, the liquid separates into two layers, the lower one consisting of dilute sulphuric acid, the upper one of a mixture in equal proportions of a sulpho-acid not decomposed by cold water and hydroxystearic acid. Approximately one-half of the sulphuric acid originally employed is always found in the lower layer.

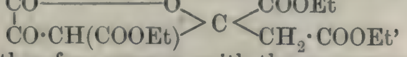
If this dilute acid is separated and an equal volume of cold water added to the remaining oil, it dissolves completely, and the solution, on standing for 12 hours at a temperature of 4°, deposits crystals of stearolactone in quantity corresponding with 18—20 per cent. of the oleic acid taken. The filtrate from the lactone, when boiled for 1 hour and allowed to stand, deposits crystals of hydroxystearic acid melting at about 80° and solidifying at 68°. If, instead of boiling the filtrate from the lactone, it is kept at a temperature of 4° or 5° for a sufficiently long time, the whole of the hydroxystearic acid will undergo conversion into stearolactone which can be separated in the crystalline state. The author is of opinion that the α-hydroxystearic acid, $C_{14}H_{29}\cdot CH_2\cdot CH_2\cdot CH(OH)\cdot COOH$, formed in the above reaction undergoes slow conversion in the cold into the γ-acid,

$$C_{14}H_{29}\cdot CH(OH)\cdot CH_2\cdot CH_2\cdot COOH,$$

which in turn furnishes the lactone. From 100 parts of oleic acid, 50 parts of solid products can be thus obtained. A. C. C.

Hazel-nut Oil. By A. SCHÖTTLER (*Chem. Centr.*, 1896, ii, 417; from *Apoth. Zeit.*, **11**, 533—534).—The oil obtained by pressing (50—55 per cent. yield) has a sp. gr. = 0·916 at 15°, Hübl's iodine number = 87, saponification number = 187, Hehner's number = 95·5, Reichert-Meissl number = 0·99 and the refractive index as determined in the butter refractometer is 1·468—1·478. The melting point of the fatty acids is 19—20°. Saponification shows that this oil contains chiefly glycerides of oleic acid with only very small quantities of palmitic acid, hence it is very similar to almond oil. E. W. W.

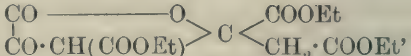
Action of Ammonia and Amines on Ethylic Oxalacetate. By WILHELM WISLICENUS and WALTER BECKH (*Annalen*, 1897, **295**, 339—366. Compare Abstr., 1895, i, 335).—Ammonia combines with ethylic oxalacetate, yielding an additive compound (*loc. cit.*); it is now found that primary and secondary bases exhibit the same behaviour, whilst tertiary amines condense with two molecular proportions of the salt without forming an additive compound. The additive compound of ammonia with ethylic oxalacetate readily decomposes forming a substance which has been hitherto regarded as ammonium triethylic aconitoxalate (compare Claisen and Hori, Abstr., 1891, 424); its behaviour, however, is more in accordance with the formula



$$\begin{array}{l} CO\text{———}O \\ \vert \\ CO\cdot CH(COOEt) \end{array}\!\!>C<\!\!\begin{array}{l} COOEt \\ CH_2\cdot COOEt \end{array}$$

and the authors therefore propose, with the concurrence of Claisen, to refer to this substance as ethylic oxalocitrolactone. The additive compounds of ethylic oxalacetate with primary and secondary amines undergo condensation on the lines of the ammonia compound, and it is noteworthy that, in the case of tertiary bases, no intermediate production of an additive compound is noticeable.

The compound of ethylic oxalacetate with ammonia develops an intense red coloration with ferric chloride; copper acetate precipitates the copper derivative of ethylic oxalacetate, whilst barium chloride gives rise to the *barium* derivative, which crystallises from hot alcohol, and melts indefinitely at 205°. Ammonium ethylic oxalocitrolactone (Abstr., 1895, 335) has been already described as arising from the foregoing compound on fusion.

Ethylic oxalocitrolactone,  $\begin{matrix}\mathrm{CO}\text{———————}\mathrm{O}\\ |\\ \mathrm{CO\cdot CH(COOEt)}\end{matrix}\!\!>\mathrm{C}<\!\!\begin{matrix}\mathrm{COOEt}\\ \mathrm{CH_2\cdot COOEt}\end{matrix}$, melts and decomposes at 213—215°, and is identical with the ethylic aconitoxalate of Claisen and Hori; it is produced on acidifying the ammonium compound, and also by the action of sodium ethoxide on ethylic oxalacetate. The *sodium* derivative develops a deep red coloration with ferric chloride.

Ethylic oxalacetate and ethylamine form an *additive compound*, which crystallises from alcohol in long, colourless needles, and melts at 107°; ferric chloride develops an intense red coloration with the aqueous solution, and copper sulphate precipitates the copper derivative of ethylic oxalacetate. On boiling the alcoholic solution, the *ethylamine* compound of ethylic oxalocitrolactone is obtained as a yellowish-brown syrup which does not solidify.

The *additive compound* of diethylamine and ethylic oxalacetate melts at 109°, and undergoes no spontaneous change; the alcoholic solution, however, when boiled, yields the *diethylamine* compound of ethylic oxalocitrolactone, which crystallises from a mixture of alcohol and ether, and melts at 126°.

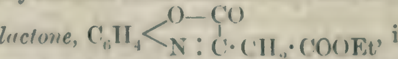
Piperidine combines with ethylic oxalacetate, and the *additive compound*, which melts at 74°, is most conveniently purified by treatment with ether on porous earthenware; the *piperidine* compound of ethylic oxalocitrolactone is produced by the spontaneous change of the foregoing substance, and melts at 93°.

When trimethylamine is passed into an ethereal solution of ethylic oxalacetate at −10°, the *trimethylamine* compound of ethylic oxalocitrolactone separates as an oil; the *triethylamine* compound is crystalline, and melts at 64°, and the *pyridine* compound at 83°. Triethylamine also precipitates a crystalline compound from an ethereal solution of ethylic dioxalosuccinolactone; it dissolves in water, and melts at 80—82°.

Benzylamine and ethylic oxalacetate combine to form an *additive compound* which melts at 88°; its behaviour, however, differs from that of the compounds already considered, as in a short time it becomes converted into dibenzyloxamide, which melts at 218°, along with the *benzylamine* salt of benzylamido-oxalic acid,

$$\mathrm{CH_2Ph\cdot NH\cdot CO\cdot COO\cdot NH_3\cdot CH_2Ph},$$

which crystallises from alcohol in white needles, and melts at 164°.

The *lactone,*  $\mathrm{C_6H_4}<\!\!\begin{matrix}\mathrm{O—CO}\\ \quad\ |\\ \mathrm{N:C\cdot CH_2\cdot COOEt}\end{matrix}$, is obtained from orthamidophenol and ethylic oxalacetate, and crystallises in slender needles melting at 102° ; it is easily resolved into its components by alcoholic soda, and does not develop any colour with ferric chloride.

M. O. F.

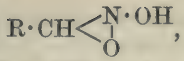
Polymethacrylic Acid. By J. ALFRED MJÖEN (*Ber.*, 1897, **30**, 1227—1240. Compare *Annalen*, 1877, **188**, 47).—The polmeride of methacrylic acid, which is formed when the latter is preserved either alone or in presence of a drop of acid, can be obtained in the anhydrous state, as a white powder, by dissolving it in alcohol and precipitating with ether. It possesses many of the properties of the colloids, and swells up before dissolving in water. It also dissolves in concentrated sulphuric acid, and is not oxidised by fuming nitric acid, potassium permanganate, or potassium dichromate. It readily dissolves in aqueous potash, requiring 1 mol. of potash for each group of the composition $C_4H_6O_2$ which is present, so that if its formula be taken as $(C_4H_6O_2)_n$ it is n-basic. When heated, it begins to decompose at 200°, and volatilises at 300° without melting ; it cannot be distilled, even in a vacuum, without undergoing complete decomposition. The determination of its molecular weight by the boiling point method, the freezing point method, and by the increase in conductivity on dilution, although not affording very consistent results, seems to point to some value in the neighbourhood of 8 for n. This result is to some extent confirmed by the fact that when the acid is titrated with baryta water, the precipitate which is formed as each drop of the alkaline solution is added at once redissolves until 2 equivalents of baryta (calculated from the simple formula $C_4H_6O_2$) have been added ; after this point, the precipitate remains undissolved and the liquid becomes neutral when 8 equivalents of baryta are present. The author therefore concludes that the acid is octobasic, having the formula $C_{24}H_{40}(COOH)_8$. and forms an acid salt in which two of the hydrogen atoms have been replaced by barium. The other salts of the acid, except those of the alkali metals, form gelatinous masses. The acid itself diffuses slowly through parchment paper. A. H.

Constitution of the Acid Amides. By WILHELM ESCHWEILER (*Ber.*, 1897, **30**, 998—1003).—When glycollic nitrile is heated with water at 130°, nitriloacetonitrile and glycollic acid are formed together with two substances, one of which melts at 55°, whilst the other melts and decomposes at 161°. The last of these has the composition $C_2H_5NO_2$, and is therefore isomeric with glycollamide, and, like this substance, yields calcium glycollate when it is heated with milk of lime. The same compound was obtained from ethylglycollimide. It differs from glycollamide, which melts without decomposition at 115—120°, in being sparingly soluble in alcohol, and in yielding a white precipitate of calcium glycollate when calcium chloride is added to its aqueous solutions.

It appears probable that this new compound represents the imido-form, $OH\cdot CH_2\cdot C(OH)\colon NH$, corresponding with glycollamide,

$OH\cdot CH_2\cdot CO\cdot NH_2$. A. H.

Acidyl Amides. By ARTHUR R. HANTZSCH (*Annalen*, 1897, **296**, 84—94. Compare Lachmann, Abstr., 1896, i, 601).—The existence of two classes of nitro-compounds having the formulæ $R\cdot CH_2\cdot NO_2$



and $R\cdot CH\Big<\begin{matrix}N\cdot OH\\ |\\ O\end{matrix}$, has been already indicated by the author (Abstr., 1896, i, 672), and an attempt is now made to apply a similar classification to the metallic derivatives of acidyl amides; according to such a scheme, these compounds would be regarded as derived from a normal amide, $R\cdot CO\cdot NH_2$, or an iso-amide, $R\cdot C(OH)\colon NH$, the corresponding thiocarbamides being expressed by the formulæ $NH_2\cdot CS\cdot NH_2$ and $NH\cdot_2C(SH)\colon NH$.

Although it has not been found possible to isolate two modifications of amides, the author is of opinion that there is sufficient evidence to justify the metallic derivatives of amides and urethane being regarded as having the metal united with oxygen; this generalisation fails, however, in the case of the mercury derivatives, it being found that the mercury derivative of acetamide has a more feeble electrical conductivity than mercuric chloride, and mercuric oxide, moreover, does not separate from an aqueous solution of the substance.

A comparison is instituted between acidyl amides and nitramide, it being shown that, whilst the former substances are neutral, exhibit feeble electrical conductivity, and do not combine directly with ammonia, nitramide has an acidic action, conducts electricity, and forms a solid ammonium derivative; this is regarded as evidence against the presence of the NH_2 group in nitramide. M. O. F.

A Higher Homologue of Carbamide. By W. OECHSNER DE CONINCK (*Compt. rend.*, 1897, **124**, 200—201).—From the urine of a patient suffering from alcoholism, the author has isolated a compound having the formula $C_4H_{10}N_2O$, which he regards as the fourth member of a homologous series commencing with carbamide. The syrupy urine is treated with 98 per cent. alcohol and filtered. The residue, after the evaporation of the alcohol, is acidified with hydrochloric acid and extracted with ether. The liquid, after neutralisation with ammonia, is treated with basic lead acetate and filtered, the excess of lead being removed from the filtrate by sulphuretted hydrogen. The filtrate from the lead sulphide, after evaporation to a syrupy consistency and extraction with absolute alcohol, consists of yellow crystals which are decolorised by means of animal charcoal. The colourless crystals thus obtained, when dried in a vacuum, melt at 270°, undergoing decomposition, and are soluble in hot water, slightly soluble in cold water and dilute alcohol, and insoluble in strong alcohol. This compound combines with acids and with metallic oxides, and undergoes decomposition with disengagement of nitrogen when heated with alkaline solutions of sodium hypochlorite. Baumstarck, in 1873, separated from the urine of an icteric patient a compound having the formula $C_3H_8N_2O$, which he regarded as the third member of the series above referred to. It is suggested that, in proportion as the oxidising power of the organism is weakened, the molecular weight of the compounds eliminated by the kidneys increases.

A. C. C.

Remarks on Zelinsky's "Researches in the Hexamethylene Series." By WLADIMIR B. MARKOVNIKOFF (*Ber.*, 1897, **30**, 1211—1214).—Claim of priority in favour of Kijner (*Journ. Russ. Chem. Ges.*, 1894,

375) respecting the recognition of "hexahydrobenzene" as methylpentamethylene (Zelinsky, this vol., i, 237). A. H.

Action of Hydriodic Acid on some Cyclic Compounds at a High Temperature. By Wladimir B. Markovnikoff (*Ber.*, 1897, 30, 1214—1221).—[In conjunction with H. Karpowitsch].—When toluene is heated with hydriodic acid, the composition of the product depends on the amount of hydriodic acid employed, the temperature, and the duration of the heating. The chief product is methylhexamethylene, smaller quantities of dimethylpentamethylene and methylpentamethylene being also formed. Heptanaphthene chloride gives the same products.

[With Retzoff and Krascheninnikoff.]—The xylenes when heated with hydriodic acid all yield toluene, whilst meta- and para-xylene in addition give a small amount of benzene. After removing the aromatic hydrocarbons, a mixture is left which consists of methylhexamethylene and methylated pentamethylenes. From the product obtained from ortho- and meta-xylene, a hydrocarbon was isolated which boils at 118—120°, has a sp. gr. = 0·7763 at 0°/0° and 0·7606 at 20°/3°. When treated with bromine, it yields tetrabromoparaxylene. No difference could be observed between the hydrocarbons yielded by the two isomerides.

When monochlorodimethylhexamethylene is heated with hydriodic acid, it yields, not only the corresponding hydrocarbon, but also products of lower boiling point, showing that decomposition has taken place.

β-Methyliodopentamethylene appears to undergo simple reduction with hydriodic acid, but the isomeric tertiary amine, $C_5H_8{:}CMe{\cdot}NH_2$, yields open chain compounds. Dimethyliodopentamethylene also yields compounds of low boiling point.

All these instances, as well as many others adduced by the author from the researches of other chemists, show that reduction with hydriodic acid at a high temperature may readily give rise to decomposition and isomerisation. Complicated side chains appear to be more readily split off than methyl, and the polymethylated cyclic compounds seem to be more easily decomposed in proportion to the number of methyl groups which they contain. A. H.

Methylcyclopentanes of Different Origin and some of their Derivatives. By Wladimir B. Markovnikoff (*Ber.*, 1897, 30, 1222—1226. Compare the foregoing abstracts).—Methylpentamethylene was prepared by the reduction of the iodide by the zinc copper couple, by heating amido-β-methylpentamethylene with hydriodic acid, and from β-methyladipic acid. On distillation with soda lime, this acid yields a *ketone* which boils at 143·5° (pressure = 738·5 mm.) and has a sp. gr. = 0·9314 at 0°/0°. The corresponding *alcohol* boils at 150·5—151° and yields methylpentamethylene when heated with hydriodic acid. The hydrocarbons obtained in these three ways appear to be identical. Methylpentamethylene boils at 71—72°, has a sp. gr. = 0·7662 at 0°/0° and smells like light petroleum. Bromine in presence of aluminium bromide converts it into an unstable crystalline compound melting at 120—121°.

[With Michail I. Konowaloff and Miller.]—The amido-compound derived from the hydrocarbon C_6H_{12} obtained from Caucasian naphtha (Abstr., 1895, i, 454), on reduction with hydriodic acid, yields a hydrocarbon boiling at 68—73°, which probably contains some hexane. A secondary nitro-compound which was also obtained yields an *amine* which boils at 120—122° and has a sp. gr. = 0·8179 at 0°/0°. The *hydrochloride* is an amorphous mass, the *platinochloride* forms dark yellow, microscopic crystals, and the *aurochloride* crystallises in lustrous, slender plates. The amide of Aschan's acid, $C_6H_{11}\cdot COOH$, yields the same secondary amine, and the acid is therefore a methylpentamethylenecarboxylic acid. Its exact constitution has not yet been determined.

Methylpentamethylene from hexamethylene.—Amidocyclohexane and chlorocyclohexane readily yield methylpentamethylene when heated with hydriodic acid. The amido-compound is not decomposed by fuming hydrochloric acid at 250°, and the chloro-derivative can be heated by itself at 250—270° without undergoing change in this direction. The isomeric change produced by the hydriodic acid is therefore not simply due to the high temperature. A. H.

Removal of Thiophen from Benzene by means of Aluminium Chloride. By Friedrich Heusler (*Zeit. angw. Chem.*, 1896, 750).—Benzene containing thiophen is heated for 9 hours in a reflux apparatus with about 5 per cent. of aluminium chloride, and then distilled without previous decantation. After washing the product with caustic soda and drying over calcium chloride, it is found to be free from thiophen.

In a previous communication (*Zeit. angw. Chem.*, 1896, 318), the author suggested that the benzene, after treatment with aluminium chloride, should be decanted and then distilled with steam. If this is done, however, traces of thiophen are always present, which is explained by supposing that an intermediate product is formed, somewhat soluble in benzene, and decomposed by water with regeneration of thiophen, but at the lower temperature it is only partially converted into a resin containing sulphur.

In the case of xylene, the temperature at which action takes place is higher, and consequently the intermediate product formed by the action of aluminium chloride on thioxen is quantitatively decomposed, so that the decanted xylene can be distilled with water without regeneration of thioxen. A. W. C.

Mass Law Studies. I. [Solubility of Benzene in Aqueous Alcohol.] By S. F. Taylor (*J. Physical Chem.*, 1897, 1, 301—303).—Varying quantities of benzene are dissolved in a given constant volume of alcohol and water added until precipitation of benzene just begins. Calling x the volume of water added and y the volume of benzene, the numbers obtained may be represented by the formula $x^{1\cdot85}y = c$. The exponent is independent of the temperature between 20° and 35°, whilst c varies with the temperature, remaining constant, however, so long as the temperature does not change. T. E.

Sulphur and Toluene. By J. K. Haywood (*J. Physical Chem*, 1897, 1, 232—233).—A mixture of sulphur and toluene, in quantities such that two liquid layers are formed, boils at 112·05°; the toluene employed boiled at 110°. With xylene boiling at 138·95°, in place of the toluene, the mixture boils at 143°. T. E.

Action of Sodium on Dibromomesitylene. By PAUL JANNASCH and W. HEUBACH (*Ber.*, 1897, **30**, 1073—1074).—By the action of sodium on dibromomesitylene in xylene solution, a new hydrocarbon is produced, which boils at 283—285° and melts at 103—104°; on bromination, it yields a *bromo*-derivative forming thin, broad needles melting at 235°, and on nitration, a *nitro*-compound crystallising from acetone in large, monoclinic prisms melting at 264—265°. The hydrocarbon is characterised by a remarkable tendency to crystallise from almost any solvent. J. F. T.

Action of Mercaptides on Quinones. By HARRY S. GRINDLEY and J. L. SAMMIS (*Amer. Chem. J.*, 1897, **19**, 290—295).—When dichlorodiphenoxyquinone (1 mol.) is treated in ethereal solution with sodium ethylmercaptide (6 mols.), a yellow, crystalline substance is obtained, which, when treated with water, dissolves, giving a clear solution; after a time, the aqueous solution undergoes decomposition, a green, crystalline substance separating, which is shown, on analysis, to be *tetrathioethylquinone*, $C_6O_2(SEt)_4$. This substance crystallises from alcohol in beautiful, glossy, dark green needles melting at 90—91°, and is soluble in concentrated nitric acid with evolution of oxides of nitrogen, imparting a beautiful red coloration to the acid, and is not reprecipitated on the addition of water.

On treatment with glacial acetic acid and zinc dust, it is reduced to *tetrathioethylquinol*, which crystallises from alcohol in large, colourless prisms melting at 58—59°. It is not acted on by concentrated hydrochloric acid, but dissolves in concentrated nitric or sulphuric acid, imparting to the former a bright red, and to the latter a light green colour.

Tetrathioethylquinonedibenzoyldithiobenzoylacetal,

$$C_6(SEt)_4(O\cdot COPh)_2(S\cdot COPh)_2,$$

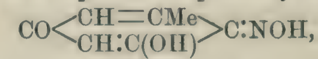
is prepared by treating the yellow, crystalline substance, obtained by the action of sodium mercaptide on tetrathioethylquinone, with benzoic chloride. It crystallises from alcohol in two distinct forms, which are easily changed one into the other. When the solution is concentrated and cooled quickly, long, slender prisms are produced, but if the solution is dilute and allowed to cool slowly, rhombic plates are obtained. Both forms melt at 131—132°. A. W. C.

Anethoil. By EDOUARD GRIMAUX (*Bull. Soc. Chim.*, 1897, [iii], **15**, 778—779).—Anethoil, $C_6H_4Pr\cdot OMe$, like other ethers, is known to absorb a large quantity of hydrogen chloride. The author has studied this reaction, but has been unable to isolate any compound. The paper also contains a note on the polymerisation of anethoil. M. W. T.

Anethoil and Two of its Homologues. By CHARLES MOUREU and A. CHAUVET (*Compt. rend.*, 1897, **124**, 404—406).—Instead of distilling methylparapropiocoumaric acid as described by Perkin (this Journal, 1877, i, 411), the authors find that anethoil can be readily prepared by heating a mixture of anisaldehyde, propionic anhydride, and fused sodium propionate in equal proportions at 200°, and that it is not necessary to first isolate the above acid. When the disengagement of carbonic anhydride has ceased, the anethoil is distilled with steam, and, after purification, first with a dilute solution of caustic soda and then with sodium bisulphite, is fractionally distilled. In a similar manner, *parabutenylanisoil*, $OMe\cdot C_6H_4\cdot CH\colon CHEt$, can be prepared by heating a mixture of anisaldehyde, butyric anhydride, and dry sodium butyrate, and is identical with the compound obtained by Perkin by the action of sodium carbonate on the additive product of methylparabutyrocoumaric acid and hydrogen iodide. The methylparabutyrocoumaric acid prepared by the authors melts at 129·5—131° (uncorr.), the melting point given by Perkin being 123°. *Paraisopentenylanisol*, $OMe\cdot C_6H_4\cdot CH\colon CHPr^{\beta}$, is obtained by heating a mixture of anisaldehyde, isovaleric anhydride, and fused sodium valerate. It has an odour of the oil of anise, boils at 248—251° (uncorr.), and has a sp. gr. = 0·977 at 0°/0°. It does not solidify even when cooled to −23°, and unites with bromine in carbon bisulphide solution. In this preparation, only traces of the unsaturated acid which is first formed could be detected amongst the products of the action. It is suggested that the characteristic odour of anethoil and of its homologues is dependent on the para-relation of the methoxy-group to the hydrocarbon chain in the molecule, and to the particular structure of this unsaturated chain.

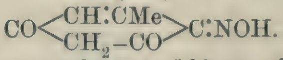
A. C. C.

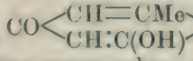
Two Modifications of Nitroso-orcinol. [Oximido-orcinol]. By Fr. Henrich (*Monatsh.*, 1897, 18, 142—188).—This paper contains a full account of an investigation, many results of which have been described already (Abstr., 1896, i, 476). The two modifications in question have the same molecular weight, as determined in acetone solution by the ebullioscopic method, and the author inclines to the opinion that they are tautomeric, and represent respectively the enolic form,



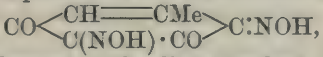
$$CO<\substack{CH=CMe\\CH\colon C(OH)}>C\colon NOH,$$

and the ketonic form, $CO<\substack{CH\colon CMe\\CH_2-CO}>C\colon NOH$. The red ($\beta$) variety is the more soluble in most solvents; 100 c.c. of ether at 22° dissolves 1·251 gram of it, but only 0·294 gram of the yellow (α) variety. Both varieties are decidedly acid, dissolving in aqueous solutions of alkali carbonates with effervescence; they can be titrated with aqueous sodium hydroxide, phenolphthalein indicating neutrality when the monosodium salt has been formed; the dissociation constant (k) of the α-variety was found to vary from 0·0330 to 0·0210 in solutions containing 1 mol. in 457 to 3656 litres. The *potassium*, *sodium*, and *silver* salts were analysed; these must contain the metal in place of the hydrogen of the NOH group, as the silver salt, when treated with methylic iodide in cooled ethereal solution, yields a yellowish *methyloximido-orcinol*, $CO<\substack{CH=CMe\\CH\colon C(OH)}>C\colon NOMe$ (melting at 117°), which loses its methoxy-group when reduced, forming amido-orcinol. A dipotassium salt could not be isolated; probably, however, it is formed to some extent in solution, for a solution of the monopotassium salt (1 mol.) and potassium hydroxide (1 mol.) has a much smaller electrical con-



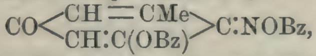


ductivity than corresponds with a simple mixture of the two substances. The further action of amylic nitrite in the presence of potassium hydroxide yields the green potassium salt of dioximido-orcinol,



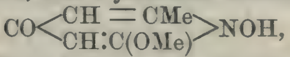
$$\mathrm{CO}\left<\begin{array}{l}\mathrm{CH{=\!=}CMe}\\ \mathrm{C(NOH)\cdot CO}\end{array}\right>\mathrm{C{:}NOH},$$

which, as is already known, is the direct product of the action of even 1 mol. only of nitrous acid on orcinol (1 mol.) in acid solution, and which is oxidised by nitric acid to dinitro-orcinol. Treatment with benzoic chloride in the presence of aqueous soda converts oximido-orcinol into a yellowish *dibenzoyl* derivative,

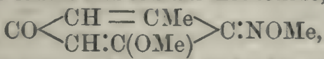


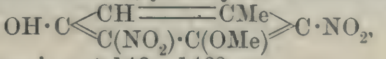
$$\mathrm{CO}\left<\begin{array}{l}\mathrm{CH=CMe}\\ \mathrm{CH{:}C(OBz)}\end{array}\right>\mathrm{C{:}NOBz},$$

melting at 157—158°. Treatment with acetic anhydride and a drop of sulphuric acid in the cold converts it into a *diacetyl* derivative melting at 119—120° (wrongly described in Abstr., 1896, i, 476, as a *mon*acetyl compound); a yellow, unstable *monacetyl* derivative, melting and decomposing at 76—77°, is formed when the potassium salt of oximido-orcinol is treated in the cold with acetic chloride in ethereal solution. By boiling orcinol in methyl-alcoholic solution with methylic iodide and sodium methoxide, and fractionating the product, *methylorcinol*, $\mathrm{OH\cdot C_6H_4Me\cdot OMe}$ [1 : 3 : 5], is obtained; this boils at 144—146° under 18 mm., at 261° under 734 mm. pressure; it is converted by nitrous acid in acid solution, or by amylic nitrite in potassium hydroxide solution, into a yellowish *oximidomethylorcinol*,



$$\mathrm{CO}\left<\begin{array}{l}\mathrm{CH=CMe}\\ \mathrm{CH{:}C(OMe)}\end{array}\right>\mathrm{NOH},$$

melting at 119—120°, and isomeric with the compound described above. This substance can also be obtained by boiling oximido-orcinol with methylic alcohol and a little hydrochloric acid; when reduced with stannous chloride, it yields a very unstable *amidomethylorcinol*, the *hydrochloride* of which, $\mathrm{C_8H_9O_2\cdot NH_2,HCl}$, was analysed; and, with methylic iodide and sodium methoxide, it yields yellow *dimethyloximido-orcinol*,  $\mathrm{CO}\left<\begin{array}{l}\mathrm{CH=CMe}\\ \mathrm{CH{:}C(OMe)}\end{array}\right>\mathrm{C{:}NOMe}$, which melts at 118°, loses one methoxy-group when reduced, forming the amidomethylorcinol just mentioned, and, when nitrated, yields yellow *dinitromethylorcinol*,



$$\mathrm{OH\cdot C}\left<\begin{array}{l}\mathrm{CH{=\!=}CMe}\\ \mathrm{C(NO_2)\cdot C(OMe)}\end{array}\right>\mathrm{C\cdot NO_2},$$

melting and decomposing at 142—143°. C. F. B.

Condensation of Methylfurfuraldehyde with Phloroglucinol. By EMIL VOTOČEK (*Ber.*, 1897, **30**, 1195—1200).—Welbel and Zeisel have shown that, under the influence of a 12 per cent. solution of hydrochloric acid, furfuraldehyde and phloroglucinol condense in the cold (Abstr., 1895, ii, 426); and the author has now studied the action of phloroglucinol on methylfurfuraldehyde, obtained by distilling rhamnose with 12 per cent. hydrochloric acid.

Methylfurfuraldehyde phloroglucide is bright red when freshly prepared, and when washed with water, and dried in air, becomes yellow; concentrated hydrochloric acid, however, renders it reddish-brown. Analysis shows it to arise either from elimination of $2H_2O$ from 4 mols. of methylfurfuraldehyde and 3 mols. of phloroglucinol, or by elimination of $3H_2O$ from 7 mols. of methylfurfuraldehyde and 6 mols. of phloroglucinol; the substance, however, does not crystallise or melt definitely. The *benzoyl* derivative is greyish-yellow. M. O. F.

Metanitrobenzyl Derivatives. By EDUARD LUTTER (*Ber.*, 1897, 30, 1065—1072).—The following derivatives are described. *Metamidobenzylic alcohol*, which is prepared from the corresponding nitro-compound by reduction with zinc and hydrochloric acid, forms long, glistening plates melting at 97°; the *monacetyl* derivative crystallises from benzene in needles melting at 106—107°, and the *diacetyl* derivative from a mixture of benzene and light petroleum in small, white needles melting at 67°; the *platinochloride* of the *monacetyl base* forms long, thin needles darkening at 196°.

Metanitrobenzylic thiocyanate, $NO_2\cdot C_6H_4\cdot CH_2\cdot SCN$ [$NO_2 : CH_2\cdot S\cdot CN = 1:3$], formed when metanitrobenzylic chloride is mixed with potassium thiocyanate in alcoholic solution, forms pale yellow, glistening needles melting at 75—76° after recrystallisation from hot alcohol. On treatment with concentrated sulphuric acid, it yields *metanitrobenzylic thiocarbamate*, $NO_2\cdot C_6H_4\cdot CH_2\cdot S\cdot CO\cdot NH_2$, which separates from amylic alcohol in small crystals melting at 121·5°; on boiling with a 20 per cent. solution of hydrochloric acid for 2 hours, this is converted into *metanitrobenzylic mercaptan*, $NO_2\cdot C_6H_4\cdot CH_2\cdot SH$, crystallising in yellowish-white needles melting at 11—12°; on oxidation with iodine, this mercaptan gives *metanitrobenzylic bisulphide*, $(NO_2\cdot C_6H_4\cdot CH_2)_2S_2$, which crystallises from alcohol in microscopic needles melting at 103—104°; and on reduction with stannous chloride yields the hydrochloride of *metamidobenzylic mercaptan*, $NH_2\cdot C_6H_4\cdot CH_2\cdot SH,HCl$, which is deposited from concentrated hydrogen chloride in small crystals melting and decomposing at 167°; the hydrochloride of *metamidobenzylic bisulphide* crystallises in small, white scales, which, however, do not melt.

Metanitrobenzylic methylic sulphide, $NO_2\cdot C_6H_4\cdot CH_2\cdot SMe$, formed when methylic alcohol reacts with metanitrobenzylic mercaptan in the presence of sodium methoxide, crystallises in long, white needles melting at 31°, and on reduction passes into the hydrochloride of *metamidobenzylic methylic sulphide*, $SMe\cdot C_6H_4\cdot NH_2,HCl$; this crystallises in colourless needles readily soluble in alcohol and amylic alcohol; the *base* is a nearly colourless oil.

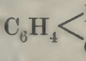
Metanitrobenzylic sulphide, $(NO_2\cdot C_6H_4\cdot CH_2)_2S$, formed when a methyl alcoholic solution of metanitrobenzylic mercaptan reacts with a methyl alcoholic solution of metanitrobenzylic chloride in the presence of sodium methoxide, crystallises from alcohol in glistening leaflets melting at 109—110°. J. F. T.

Cholesterol. By CH. CLOËZ (*Compt. rend.*, 1897, **124**, 864—866).—When a solution of bromine in carbon bisulphide is gradually added to a solution of cholesterol in the same solvent, both being cooled to −15°, the liquid suddenly becomes filled with minute, acicular crystals which redissolve as the addition of bromine is continued, the cholesterol being converted into the dibromide $C_{26}H_{44}OBr_2$. The crystalline precipitate is readily isolated, and has the empirical composition

$C_{26}H_{44}OBr$, but it is really a molecular compound of cholesterol and its dibromide, $C_{26}H_{44}OBr_2,C_{26}H_{44}O$, and can be formed by mixing, at $-15°$, molecular proportions of its proximate constituents dissolved in carbon bisulphide. It melts and decomposes at 112°, is very soluble in chloroform, ether, and benzene, and also in carbon bisulphide except at low temperatures. It is only slightly soluble in alcohol at the ordinary temperature, but dissolves readily at 70°, and this fact can be utilised for purifying the compound. Attempts to separate the compound into its components by the action of various solvents gave negative results; it either remained unaltered, or was converted into resinous products, especially if heated. C. H. B.

Carbamide Derivatives of Orthoamidobenzylamine. By Carl Paal and Br. Hildenbrand (*J. pr. Chem.*, 1897, [ii], **55**, 238—248). —Diphenylorthoamidobenzylcarbamide,

$$NH_2\cdot C_6H_4\cdot CH_2\cdot NPh\cdot CO\cdot NHPh$$

(Abstr., 1891, 944; 1894, i, 186), can be obtained by reducing the nitro-compound either with tin and hydrochloric acid in alcoholic solution or with zinc and acetic acid. The yellow *platinochloride*, $(C_{20}H_{19}N_3O)_2,H_2PtCl_6$, melts at 187°; the *stannochloride* decomposes at 172°, and is partially decomposed by water; the yellow *picrate*, $C_{20}H_{19}N_3O,C_6H_3N_3O_7$, melts at 164°. With acetic anhydride at the ordinary temperature, it yields an *acetyl* derivative, melting at 145°, and when warmed with benzoic acid for a few minutes, a *benzoyl* derivative melting at 170°. When warmed with phenylic cyanate in benzene solution, it is converted almost quantitatively into *orthophenylureidobenzyldiphenylcarbamide*, $NHPh\cdot CO\cdot NH\cdot C_6H_4\cdot CH_2\cdot NPh\cdot CO\cdot NHPh$, which melts at 139—140°, and when heated above its melting point, decomposes into diphenylcarbamide and *3′-phenyl-2′-ketotetrahydroquinazoline*,  $C_6H_4<\begin{matrix}NH\cdot CO\\ CH_2\cdot NPh\end{matrix}$, which melts at 186—188°. With phenylic thiocyanate, an analagous *thio*-compound, melting at 222°, is formed, but this yields no quinazoline when heated.

Phenylorthoamidobenzylparatolylcarbamide,

$$NH_2\cdot C_6H_4\cdot CH_2\cdot N(C_6H_4Me)\cdot CO\cdot NHPh$$

(Abstr., 1894, i, 187), yields a similar series of compounds, of which the names and melting points are here given. *Stannochloride*, 174°; *hydrochloride*, $C_{21}H_{21}N_3O,HCl$, 156°; *platinochloride*,

$$(C_{21}H_{21}N_3O)_2,H_2PtCl_6,$$

yellow, 183°; *oxalate*, $C_{21}H_{21}N_3O,C_2H_2O_4 + 3\frac{1}{2}H_2O$, 166° (when anhydrous); *picrate*, $C_{21}H_{21}N_3O,C_6H_3N_3O_7$, yellow, 156°. *Acetyl*, 141°, and *benzoyl*, 192—193°, derivatives. *Ureido*-compound, 135°; *3′-paratolyl-2′-ketotetrahydroquinazoline*, 218°. *Thioureido*-compound, 230—231°.
C. F. B.

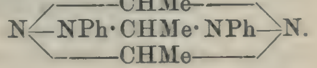
Halogenated Diazonium Chlorides. By Benno Hirsch (*Ber.*, 1897, **30**, 1148—1153).—Pure, neutral, halogenated diazonium chlorides are only obtained from the hydrochlorides of chlor-, brom-, or iod-aniline, on treatment with amylic nitrite, when the former are absolutely free from the last traces of free acid, so that in the preparation of the following compounds it was found necessary to prepare the hydrochlorides by passing dry hydrogen chloride into a solution of the amine in absolute alcohol, and then to heat the product at 30—40°, until the last traces of acid had been removed. *Parabromodiazonium chloride* consists of fine, white crystals, which are somewhat hygroscopic, the *pariodo*-compound forming white needles, very insoluble in absolute alcohol. *Orthochlorodiazonium chloride*, and *metachlorodiazonium chloride* are white, crystalline, neutral salts; nitrogen is slowly eliminated from the ortho- and meta-compounds in alcoholic solutions, but the *para*-derivative is stable. J. F. T.

Acid Diazonium Chlorides. By ARTHUR R. HANTZSCH (*Ber.*, 1897, **30**, 1153—1158).—There are two types of acid diazonium chlorides, namely the mon-acid salt, $R\cdot N_2Cl,HCl$, and the tri-acid salt, $3RN_2Cl,HCl$, *tri-acid parabromodiazonium chloride*, $3C_6H_4Br\cdot N_2Cl,HCl$, formed when the diazotisation is carried out in presence of excess of hydrochloric acid, crystallises in needles. The *tri-acid trichlorodiazonium chloride*, $3C_6H_2Cl_3\cdot N_2Cl,HCl$, is formed in the same way.

Monacid tribromobenzenediazonium chloride, $C_6H_2Br_3\cdot N_2Cl,HCl + 4H_2O$, forms white, microscopic crystals readily soluble in water, and shows all the reaction of a diazonium salt. J. F. T.

Two Isomeric Triethylidenediphenylhydrazines. By HENRI E. CAUSSE (*Compt. rend.*, 1897, **124**, 197—200).—*α-Triethylidenediphenylhydrazine*, $C_{18}H_{22}N_4$, is formed when a solution of acetaldehyde in aqueous phosphoric acid (24·6 grams H_3PO_4 per litre) is added to a solution of sodium thiosulphate (25 grams) in water (500 c.c.) containing 20 grams of phenylhydrazine. The crystals which separate are washed with water, dried, treated with alcohol, and filtered in order to remove the insoluble isomeride. The alcoholic solution on evaporation leaves a crystalline mass of the α-compound, which, when washed with ether and dried in an atmosphere of carbonic anhydride, melts at 60°. When exposed to the air, it increases in weight and becomes yellow. It is but slightly soluble in cold water, dissolves in alcohol and ether; less readily in benzene and light petroleum. From hot water, it separates in colourless, leaf-like crystals. It does not reduce Fehling's solution, and is not acted on by caustic alkalis; but reduces solutions of mercuric chloride and silver nitrate. With acid chlorides, it reacts with difficulty, substitution products of phenylhydrazine being formed. On mixing alcoholic solutions of this compound and of benzaldehyde, *dibenzylidenediphenylhydrazine*, $C_{26}H_{24}N_4 + \frac{1}{2}H_2O$, separates out after some days in long needles melting at 156°. *β-Triethylidenediphenylhydrazine* is prepared by adding a mixture of acetaldehyde (25 grams), normal aqueous phosphoric acid (50 grams), and water (175 grams) gradually to a mixture of normal phosphoric acid (825 grams), glycerol (150 grams), and phenylhydrazine (20 grams). A granular precipitate consisting of both isomerides is formed, from which the β-compound can be obtained by washing first with water, and then with alcohol. From boiling alcohol, it separates in colourless prisms melting at 99·5°, which are stable in the air, very slightly soluble in hot, insoluble in cold water, and but slightly soluble in alcohol, benzene, and ether in the cold. It is very stable, being practically unacted on by acids, alkalis, acid chlorides, and benzaldehyde, and does not reduce Fehling's solution. The author is of opinion that these two isomerides have the following formulæ:

(α) $CHMe(NPh\cdot N:CHMe)_2$. (β)



$$N\begin{cases}-CHMe-\\-NPh\cdot CHMe\cdot NPh-\\-CHMe-\end{cases}N.$$

A. C. C.

Unsymmetrical Phenylhydrazine Derivatives. By Hans Rupe and Joh. Všetečka (*Ber.*, 1897, 30, 1101. Compare Abstr., 1895, i, 521; 1896, i, 429).—Chloracetodimethylparaphenylenediamine (m. p. 146—147°) obtained by the action of chloracetic chloride on dimethylparaphenylenediamine, reacts with phenylhydrazine, yielding *phenylhydrazido-acetodimethylparaphenylenediamine*,

$$NH_2\cdot NPh\cdot CH_2\cdot CO\cdot NH\cdot C_6H_4\cdot NMe_2,$$

which crystallises in yellowish needles, and melts at 134—135°. The compounds with benzaldehyde, ethylic acetoacetate, and acetic chloride melt respectively at 184—185°, 185°, and 158°. Its nitroso-derivative, $NO\cdot NPh\cdot CH_2\cdot CO\cdot NH\cdot C_6H_4\cdot NMe_2$, melting at 165°, is identical with that obtained from anilidoacetodimethylparaphenylenediamine (m. p. 132—134°). J. J. S.

The Ketonehydrazones of Aromatic Hydrazines. By August Arnold (*Ber.*, 1897, 30, 1015—1017).—Acetonephenylhydrazone reacts vigorously with phenylcarbimide to form a compound which melts at 196°, and is very sparingly soluble in the ordinary solvents. The same substance appears to be formed in a similar way from the phenylhydrazone of methyl ethyl ketone, and from ethylidenephenylhydrazone, but its constitution has not yet been ascertained. Acetone phenylhydrazone readily combines with isocyanic acid to form *acetonephenylhydrazonesemicarbazide*, $NH_2\cdot CO\cdot NPh\cdot N:CMe_2$, which crystallises in white needles melting at 140°. When boiled with water, it yields acetone and phenylhydrazinesemicarbazide.

Methylethylketonephenylhydrazone-thiosemicarbazide,

$$NHPh\cdot CS\cdot NPh\cdot N:CMeEt,$$

crystallises in slender needles melting at 174°. The corresponding *semicarbazide* forms slender plates melting at 168°.

Acetoneparatolylhydrazone hydrochloride crystallises in slender needles melting at 135°, whilst the *hydrobromide* melts at 195°; the *nitrate* is also a crystalline substance. The *phenylthiosemicarbazide*,

$$NHPh\cdot CS\cdot N(C_6H_4Me)N:CMe_2,$$

forms white needles melting at 164°. A. H.

Phenylnitromethane [exo-Nitrotoluene]. By Arnold F. Holleman (*Rec. trav. Chim.*, 1896, 15, 356—364, 365—369. Compare Abstr., 1895, i, 455, and 1896, i, 148).—Benzoic chloride reacts with a methylic alcoholic solution of sodium phenylnitromethane, yielding dibenzhydroxamic acid, the melting point of which the author gives as 161°, and not 153°. Paranitrobenzoic chloride reacts with sodium phenylnitromethane suspended in dry benzene, yielding a mixture of *dinitrodibenzoylbenzhydroxamic acid*,

$$NO_2\cdot C_6H_4\cdot CO\cdot O\cdot CPh:NO\cdot CO\cdot C_6H_4\cdot NO_2,$$

and *nitrobenzoylhydroxamic acid*, $OH\cdot CPh:NO\cdot CO\cdot C_6H_4\cdot NO_2$. These two compounds are readily separated by N/10 sodium hydroxide, which dissolves the mononitro-derivative melting at 168°, and leaves the dinitro-derivative; the latter, after crystallisation from benzene, melts at 187°; it is probably contaminated with a small quantity of paranitrobenzoic anhydride, which melts at 186°. The dinitro-derivative, when heated in a sealed tube with concentrated hydrochloric acid, decomposes, yielding benzoic and paranitrobenzoic acids.

Benzoylnitrobenzhydroxamic acid, $NO_2\cdot C_6H_4\cdot C(OH){:}NOBz$, obtained by the action of benzoic chloride on potassium paranitrophenylnitromethane, crystallises from its acetic acid solution in colourless plates, and melts and decomposes at 187°. When heated with concentrated hydrochloric acid at 150—160° for 3 hours, it is completely decomposed into hydroxylamine, benzoic acid, and paranitrobenzoic acid. It is readily soluble in alkalis, and is precipitated unaltered on the addition of acids, but if the precipitate is left in contact with the acid liquid for several hours, it is gradually transformed into an isomeric compound sparingly soluble in alkalis.

Paranitrophenylnitromethane [*ω*: *4-dinitrotoluene*] $NO_2\cdot C_6H_4\cdot CH_2\cdot NO_2$, obtained by the action of paranitrobenzylic iodide on silver nitrite, crystallises in glistening plates, and melts at 90°. The *potassium* derivative, $NO_2\cdot C_6H_4\cdot CHK\cdot NO_2 + 2H_2O$, is very characteristic, crystallising in small, glistening, red crystals. *Orthonitrophenylnitromethane* [*ω*: *2-dinitrotoluene*], obtained in a similar manner, melts at 72°, and also yields a potassium derivative with $1H_2O$, crystallising in glistening, red needles. J. J. S.

Action of Sodium Ethoxide on Bromamides. By S. E. Swartz (*Amer. Chem. J.*, 1897, **19**, 295—319).—Sodium ethoxide in alcoholic solution acts on amides and bromamides in two ways; firstly, as a reducing agent, thereby regenerating the acid amide, and secondly as a rearranging agent, changing the amidobromide to a bromoformamide or carbimide. The latter may react with the alcohol present, forming a urethane, or with the acid amide, generated by the reduction of the bromamide forming a substituted carbamide; or it may be hydrolysed, thus producing an amine. The products of the change depend on the concentration of the solution and on the nature of the bromamide used. In concentrated solution, the acid amide is regenerated, whilst in more dilute solutions, rearrangement, with the formation of urethanes or ureas, takes place; and in very dilute solutions hydrolysis of the carbimide occurs, with the production of an amine.

When sodium methoxide acts on succinimide bromide in benzene solution, 70 per cent. of the theoretical amount of succinimide and a considerable amount of tar are produced, but no urethane or substituted hydroxylamine. If sodium ethoxide is used, varying amounts of succinimide and diethylic succino-β-ureidopropionate melting at 78° are formed.

When benzamide bromide is slowly added to a well-cooled solution of sodium ethoxide in absolute alcohol, reaction takes place slowly, as indicated by a gradual rise in temperature; the solution becomes brownish red, and on cooling benzoylphenylcarbamide separates, whilst the alcoholic mother liquor contains phenylurethane and benzamide.

The action of sodium ethoxide on the isomeric nitrobenzamide bromides has also been studied. The para-compound yields paranitrophenylurethane, paranitrobenzoylparanitrophenylcarbamide, and paranitrobenzamide; and the ortho- and meta-compounds, the corresponding ortho- and meta-urethanes, carbamides, and amides.

The author has examined the action of phosphorus pentachloride on the nitrophenylurethanes produced in the above experiments in order to ascertain if the production of chloro-formamides and carbimides by the reaction is a general one, and also for the closer investigation of the properties of such substances.

When phosphorus pentachloride and methylorthonitrophenylurethane are mixed in molecular proportion and gently warmed, reaction takes place, and methylic chloride is disengaged. The slightly yellowish liquid product, when cooled in a freezing mixture, deposits needle-shaped crystals melting at 47°, which prove to be chloro-formorthonitranilide.

If, instead of isolating the chloroformorthonitranilide as above, the phosphorus oxychloride is distilled off in a current of dry hydrogen chloride, and the residue heated in a current of dry air until no more hydrogen chloride is given off, orthonitrophenylcarbimide is formed, which may be extracted with light petroleum. It crystallises readily in clusters of delicate, needle-shaped crystals, and melts at 41°. With water, it yields nitraniline, and with ethylic and methylic alcohols it gives the corresponding urethanes. When left for some time in a vacuum, it is changed into a crystalline substance melting at 220°, which is probably a cyanurate. The same substance is produced when chloroformorthonitranilide is allowed to remain for some time.

Isopropylic orthonitrophenylcarbamate, $NO_2{\cdot}C_6H_4{\cdot}NH{\cdot}COOPr^\beta$, is formed by the interaction of isopropylic alcohol and orthonitrophenylcarbimide; it crystallises from light petroleum in yellow cubes, which melt at 12°. The corresponding *isobutyl* derivative forms yellow crystals melting at 13°, the *normal amyl* derivative crystals melting at −5°.

Glycol nitrophenylmonocarbamate, $NO_2{\cdot}C_6H_4{\cdot}NH{\cdot}COO{\cdot}C_2H_4{\cdot}OH$, a yellow, crystalline substance melting at 71° without decomposition, is formed by the action of glycol on the above-mentioned carbimide; it is not affected by cold alkalis or dilute acids, but, on heating, they readily decompose it. By varying the proportions of glycol and carbimide, the glycol dicarbamate can be obtained as a yellow, crystalline substance melting at 160°.

Orthonitrocarbanilide, $NO_2{\cdot}C_6H_4{\cdot}NH{\cdot}CO{\cdot}NHPh$, is obtained as an almost white, crystalline substance melting at 170°, when the carbimide is treated with the molecular quantity of aniline in ethereal solution.

Orthonitrophenylcarbamide, $NO_2{\cdot}C_6H_4{\cdot}NH{\cdot}CO{\cdot}NH_2$, is formed when an ethereal solution of orthonitrophenylcarbimide is saturated with dry gaseous ammonia; the crystals melt at 181°.

Symmetrical orthonitrophenylorthotolylurea,

$$NO_2{\cdot}C_6H_4{\cdot}NH{\cdot}CO{\cdot}NH{\cdot}C_6H_4Me,$$

is obtained as a crystalline substance melting at 189° when orthotoluidine acts on orthonitrophenylcarbimide in ethereal solution. It closely resembles orthonitrocarbanilide in all its properties.

Orthonitrophenyldimethylcarbamide, $NMe_2·CO·NH·C_6H_4·NO_2$, is formed when dry methylamine is passed into an ethereal solution of orthonitrophenylcarbimide, warmed until a test with aniline gives no precipitate of orthonitrocarbanilide; it is an oil which does not solidify at −30°. The corresponding *diethyl*, *dipropyl*, *dibutyl*, and *diamyl* compounds are all oils, formed by methods precisely similar to the above.

Chloroformoparanitranilide, prepared in the same manner as the corresponding ortho-compound, is a white substance with a very penetrating odour. When heated, it loses hydrogen chloride, and at 75° is converted into the carbimide.

Paranitrophenylcarbimide, prepared as above, crystallises from light petroleum in concentric clusters of white needles which melt at 44°. Water decomposes it, giving nitraniline, and with amines and alcohols carbamides and urethanes are formed. On standing, it is polymerised, the change being hastened by heating.

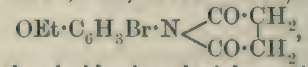
Isopropylparanitrophenylurethane, formed by the interaction of isopropylic alcohol and this carbimide, melts at 78°; the corresponding isobutyl compound melts at 62°.

Paranitrocarbanilide is obtained as a precipitate melting at 209°, when aniline is added to an ethereal solution of paranitrophenylcarbimide. A. W. C.

Hydrolysis of Acid Amides. By IRA REMSEN (*Amer. Chem. J.*, 1897, **19**, 319–321).—The relative ease with which the three nitrobenzamides are converted into their ammonium salts by dilute acids has been studied. The results obtained show that the ortho-amide resists the action of the hydrolysing agent to a marked degree, whereas the meta- and para-amides are readily affected, the para somewhat more so than the meta.

The author proposes investigating the method more fully in order to ascertain whether the influence of ortho-groups on the hydrolysis of acid amides is always the same; and how various atoms and groups differ in their effect on the rate of hydrolysis. A. W. C.

Orthobromoparethoxyphenylsuccinimide (Bromopyrantine). By ARNALDO PIUTTI (*Ber.*, 1897, **30**, 1170—1174).—*Orthobromoparethoxyphenylsuccinimide*,



$OEt·C_6H_3Br·N<\begin{matrix}CO·CH_2\\ |\\ CO·CH_2\end{matrix}$, obtained by the action of bromine on the imide in glacial acetic acid, crystallises from alcohol in colourless needles melting at 150—151°; when heated with concentrated hydrochloric acid in a reflux apparatus, it yields orthobromoparaphenetidine hydrochloride. The free base, which has been recently described by Hodurek (this vol., i, 276), crystallises in the rhombic system; $a:b:c = 0·7425:1:0·8433$. The *phthalyl* derivative crystallises in colourless needles melting at 195—196°; it is produced by the action of phthalic anhydride on the base, and is also formed when bromine acts on parethoxyphenylphthalimide. The *succinyl* derivative melts at 150—151°.

Orthobromoparethoxyphenylsuccinamic acid,

$OEt{\cdot}C_6H_3Br{\cdot}NH{\cdot}CO{\cdot}C_2H_4{\cdot}COOH$,

is produced when the imide is hydrolysed with alcoholic potash, and crystallises from alcohol in white needles melting at 149—150°; the *silver* salt is crystalline.

Orthobromoparaphenetidine hydrochloride has more pronounced toxic properties than phenacetine and pyrantine; it also acts vigorously on blood, and converts oxyhæmoglobin into methæmoglobin. Orthobromoparethoxyphenylsuccinimide, however, does not give rise to functional derangement, probably owing to its insoluble character.

M. O. F.

2:5-Dichlorobenzaldehyde. By ROBERT GNEHM and EMIL BÄNZIGER (*Annalen*, 1897, **296**, 62—84. Compare Abstr., 1896, i, 432).—The main facts recorded in this paper have already appeared (*loc. cit.*)

M. O. F.

Salicylaldehyde. By FRITZ BLAU (*Monatsh.*, 1897, **18**, 123—137).—The substance obtained by Möhlau (Abstr., 1886, 1033), by condensing salicylaldehyde with aniline in the presence of zinc chloride, is, as he thought, acridine, and not phenanthridine. A better yield is obtained by using ready-formed "salhydranilide" ($OH{\cdot}C_6H_4{\cdot}CH{:}NPh$), with phosphoric anhydride as a condensing agent, but even then the yield is extremely small.

When an attempt was made to use strong sulphuric acid as a condensing agent, and salhydranilide was heated with five times its weight of the acid for an hour on the water bath, *orthohydroxybenzylideneanilinesulphonic acid*, $OH{\cdot}C_6H_3(SO_3H){\cdot}CH{:}NPh$, was formed; this crystallises from water in yellow needles containing $1H_2O$; its solution in water is less yellow than those of its salts; of these, the crystalline *sodium*, $C_{13}H_{10}NSO_4Na,C_{13}H_{11}NSO_4$; *barium*, $(C_{13}H_{10}NSO_4)_2Ba + 4H_2O$, and *silver*, $C_{13}H_{10}NSO_4Ag + 2H_2O$ (or anhydrous) salts were prepared. These are much less stable than the free acid, and decompose readily in aqueous solution into aniline and salts of *salicylaldehydesulphonic acid*, $OH{\cdot}C_6H_3(SO_3H){\cdot}CHO$. This acid is best prepared by boiling salhydranilide with baryta water or with aqueous sodium carbonate; the *sodium*, $C_7H_5SO_5Na + 2H_2O$; *barium*, $(C_7H_5SO_5)_2Ba + H_2O$ and $C_7H_4SO_5Ba + 3H_2O$, and *silver*, $C_7H_5SO_5Ag$, salts were prepared and analysed. With phenylhydrazine, the acid yields the *phenylhydrazine* salt of the *phenylhydrazonesulphonic acid*, $C_{19}H_{20}N_4O_4S$, and it is oxidised by silver oxide to the acid $OH{\cdot}C_6H_3(SO_3H){\cdot}COOH$, obtained by direct sulphonation of salicylic acid; this acid yields no azo-dyes with diazochloride solutions, from which circumstance it is inferred that the para-position relative to the hydroxyl group is occupied, in which case the acid must have the composition $[COOH : OH : SO_3H = 1 : 2 : 5]$. This is the first time that a sulphonic acid of salicylaldehyde has been prepared.

C. F. B.

Some Derivatives of Salicylaldehyde. By PAUL RIVALS (*Compt. rend.*, 1897, **124**, 368—370).—The author confirms Etting's statement that the compound of salicylaldehyde and caustic potash, $C_7H_6O_2,KOH$, loses water in a vacuum at 120°, yielding the derivative

$C_7H_5O_2K$. The following numbers for the heat of formation of this compound are given:

$C_7H_6O_2$ liq. + KOH sol. = $C_7H_5O_2K,H_2O$ sol. …… + 18·6 Cal.
$C_7H_6O_2$ liq. + KOH sol. = $C_7H_5O_2K$ sol. + H_2O sol. + 21·5 Cal.

the latter number being identical with the heat of formation of the isomeric benzoate, and much higher than that of the phenoxides. By the action of acetic chloride on salicylaldehyde, the author has obtained both acetosalicyl (melting at 35° and boiling at 253°) and parasalicyl as described by Perkin. The molecular weight of parasalicyl determined by the cryoscopic method agrees with the formula $C_{14}H_{10}O_3$. Its molecular heat of combustion is 1589·7 Cal. (const. volume) and 1590·3 Cal. (const. pressure), the deduced heat of formation of solid parasalicyl from its elements being + 74·9 Cal. Its heat of formation from the aldehyde would be:

$2C_7H_6O_2$ liq. = $C_{14}H_{10}O_3$ sol. + H_2O sol.… + 26·2 Cal.

Since all anhydrides are formed from their elements with absorption of heat, the above number is incompatible with the constitutional formula $CHO\cdot C_6H_4\cdot O\cdot C_6H_4\cdot COH$ assigned to parasalicyl by Perkin. The ease with which dialdehydes undergo transformation into unsymmetrical compounds with development of heat renders it probable that parasalicyl is such a compound. A. C. C.

Derivatives of Acetophenone. By SIEGMUND GABRIEL and GEORG ESCHENBACH (*Ber.*, 1897, **30**, 1126—1129).—A slightly acidified solution of ω-amido-acetophenone hydrochloride, when treated with sodium amalgam (2½ per cent.), yields acetophenone and ammonia. The oxime of ω-phenoxyacetophenone (Fritz, Abstr., 1896, i, 151), when reduced with sodium amalgam and alcohol, yields phenol and α-phenylethylamine, $NH_2\cdot CHMePh$.

ω-Amido-acetophenoneoxime crystallises in reddish-yellow, flat needles and melts at 140°. The authors have prepared ω-cyanacetophenone by the action of an alcoholic solution of potassium cyanide on ω-bromacetophenone; the yield is 60 per cent. of the theoretical. When the cyano-derivative is reduced with sodium amalgam, it yields the nitrile of β-phenyl-β-lactic acid, $OH\cdot CHPh\cdot CH_2\cdot CN$, which, when further reduced with sodium and alcohol, yields phenylpropylamine. The hydroxy-nitrile combines apparently with hydrogen bromide yielding a *compound*, $C_9H_9NO + 2HBr$, which melts at 116°. Concentrated hydrochloric acid in the cold hydrolyses the hydroxy-nitrile with formation of *β-phenyl-β-lactamide*, $OH\cdot CHPh\cdot CH_2\cdot CO\cdot NH_2$, which melts at 119—120°. The amide, when heated with hydrochloric acid (15 per cent.), yields cinnamic acid. J. J. S

Action of Alcohols on Isoimides. By P. HOJONIDES VAN DER MEULEN (*Rec. trav. Chim.*, 1896, **15**, 323—348. Compare this vol., i, 281).—Alcohols as a rule react with isoimides or their hydrochlorides (Abstr., 1896, i, 314), yielding the corresponding ethereal salts of the amido-acids. Methylic alcohol reacts with α-camphorisoimide hydrochloride, forming methylic α-camphoramate, $NH_2\cdot CO\cdot C_8H_{14}\cdot COOMe$, which melts at 152—153°; the same salt is obtained when hydrogen chloride is passed into a solution of cyanolauronic acid (Oddo and Leonardi, this vol., i, 86).

Methylic α-camphormethylamate, $NHMe{\cdot}CO{\cdot}C_8H_{14}{\cdot}COOMe$, melts at 135—136°. *Methylic β-camphoramate*, which may be obtained either from β-camphorisoimide hydrochloride, or by passing hydrogen chloride into a methyl alcoholic solution of β-camphoramic acid, can be crystallised from water, melts at 138—142°, and is readily hydrolysed. The corresponding *ethylic* salt melts at 94°.

Methylic β-camphormethylamate, obtained from β-camphormethylamic acid, melts at 68°; it is best isolated by the addition of light petroleum to its benzene solution.

Methylic β-hemipinamate, $C_6H_2(OMe)_2(COOMe){\cdot}CONH_2$ [3 : 4 : 1 : 2], can be obtained from β-hemipinisoimide or from cyanodimethoxybenzoic acid, [OMe_2 : COOH : CN = 3 : 4 : 1 : 2] (Abstr., 1896, i, 315); it melts at 173—174°.

Ethylic β-hemipinamate melts at 180—181°, and is at the same time converted into the imide.

Methylic α-hemipinobenzylamate, $C_6H_2(OMe)_2(CO{\cdot}NH{\cdot}C_7H_7){\cdot}COOMe$ [3 : 4 : 1 : 2], melts at 96—97°, and the *methylic* salt of the corresponding β-acid at 113°.

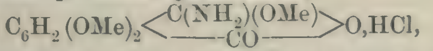
Methylic succinophenylamate, $COOMe{\cdot}C_2H_4{\cdot}CO{\cdot}NHPh$, was obtained from succinophenylamic acid by first converting it into its isoimide, and treating the latter with methylic alcohol; it is thrown down from its acetone solution on the addition of water, and melts at 91—96°. *Methylic succinobenzylamate*, $COOMe{\cdot}C_2H_4{\cdot}CO{\cdot}NH{\cdot}C_7H_7$, when precipitated from its benzene solution by the addition of light petroleum, melts at 61—64°. *Methylic phthalophenylamate*,

$$COOCH_3{\cdot}C_6H_4{\cdot}CO{\cdot}NHPh,$$

melts at 111—113·5°, and is readily soluble in most organic solvents with the exception of light petroleum.

Certain isoimide hydrochlorides react with alcohols, yielding substances isomeric with the normal ethereal salts, whilst in other cases the product consists of a mixture of the normal and iso-ethereal salt, for example, phthalophenylisoimide.

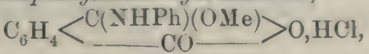
Iso-methylic α-hemipinamate hydrochloride,



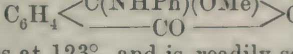
$$C_6H_2(OMe)_2<\!\begin{array}{c}C(NH_2)(OMe)\\ \hline CO\end{array}\!>O,HCl,$$

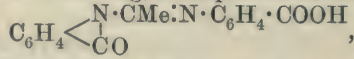
melts and decomposes at about 141°, and is readily soluble in water and in alkali hydroxides or carbonates. The same compound is formed when cyanodimethoxybenzoic acid, [$(OMe)_2$: CN : COOH = 3 : 4 : 1 : 2] (Abstr., 1896, i, 315), is dissolved in methylic alcohol and the solution saturated with hydrogen chloride. It yields an *aurochloride* crystallising in yellow plates. The hydrochloride, when treated with potassium nitrite, yields α-methylic hemipinate melting at 120—122°.

Iso-methylic phthalophenylamate hydrochloride,

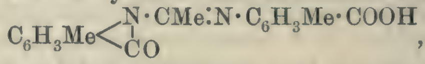


$$C_6H_4<\!\begin{array}{c}C(NHPh)(OMe)\\ \hline CO\end{array}\!>O,HCl,$$

obtained by the action of methylic alcohol on phthalophenylisoimide hydrochloride, is decomposed by cold water, yielding the free *isomethylic* salt,  $C_6H_4<\!\begin{array}{c}C(NHPh)(OMe)\\ \hline CO\end{array}\!>O$, or $COOH{\cdot}C_6H_4{\cdot}C(OMe){:}NPh$, which melts at 123°, and is readily soluble in alkalis or alkali carbonates. The hydrochloride is readily decomposed by boiling water, yielding *phthalophenyldiamide*, which is insoluble in the usual solvents, but crystallises from nitrobenzene in small needles melting at 251—252°. The *silver* salt of the isomethylic salt is also described. J. J. S.

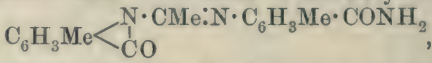
Amidines of the Anthranilic Acids. By M. KOWALSKI and STEFAN VON NIEMENTOWSKI (*Ber.*, 1897, **30**, 1186—1193).—*Ethenyldianthranilic acid*, $COOH\cdot C_6H_4\cdot NH\cdot CMe{:}N\cdot C_6H_4\cdot COOH$, is obtained by hydrolysing the anhydride with aqueous sodium carbonate, and crystallises in long, transparent needles melting at 226°. The *anhydride*,  $C_6H_4<\begin{array}{l}N\cdot CMe{:}N\cdot C_6H_4\cdot COOH\\ |\\ CO\end{array}$, is produced on heating acetanthranilic acid with acetic anhydride ($2\frac{1}{2}$ mols.) during 50 hours; the liquid is poured into water, and the precipitate extracted with boiling water to remove unaltered acetanthranilic acid, the residue being finally crystallised fractionally from alcohol. The anhydride separates from glacial acetic acid in white scales, softens at 240°, and melts at 248°.

The *anhydride* of ethenyldimetahomoanthranilic acid,



$$C_6H_3Me<\begin{array}{l}N\cdot CMe{:}N\cdot C_6H_3Me\cdot COOH\\ |\\ CO\end{array},$$

is formed when metahomoanthranilic acid is treated with boiling acetic anhydride, and crystallises from alcohol in white scales melting at 293°; it is insoluble in water and ether, and dissolves very sparingly in boiling benzene; when treated with boiling alkalis, it yields metahomoanthranilic acid. The *amide* of the anhydride,



$$C_6H_3Me<\begin{array}{l}N\cdot CMe{:}N\cdot C_6H_3Me\cdot CONH_2\\ |\\ CO\end{array},$$

is produced simultaneously with the foregoing substance, from which it may be separated by its more sparing solubility in alcohol; it crystallises in somewhat indefinite brown scales, and melts at 278°. Boiling caustic soda converts the amide into a *compound* which crystallises from alcohol in long, lustrous needles and melts at 235—240°.

Pyruvodianthranilic acid,

$$COOH\cdot C_6H_4\cdot N{:}C(COMe)\cdot NH\cdot C_6H_4\cdot COOH,$$

is prepared by heating anthranilic and pyruvic acids with toluene in a reflux apparatus; it crystallises from alcohol in small, yellowish needles, and melts at 295°. The *phenylhydrazone* softens at 165—170°, and melts and effervesces at 250°.

Pyruvodimetahomoanthranilic acid,

$$COOH\cdot C_6H_3Me\cdot N{:}C(COMe)\cdot NH\cdot C_6H_3Me\cdot COOH,$$

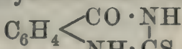
crystallises from water or alcohol in straw yellow needles, and melts, decomposing, at 280°. The *phenylhydrazone* forms bright yellow needles and softens at 202°; it melts and decomposes at 206°.

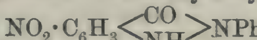
M. O. F.

Anthranilic Acid Derivatives. By HANS RUPE (*Ber.*, 1897, **30**, 1097—1100).—Anthranilic acid cannot be directly nitrated; acetylanthranilic acid, however, when dissolved in concentrated sulphuric acid, and then treated with a mixture of nitric (sp. gr. 1·44) and sulphuric acids, yields *metanitroacetanthranilic acid*,

$$NO_2\cdot C_6H_3(NHAc)\cdot COOH.$$

This acid crystallises from its hot, aqueous solution in yellow needles and melts at 152°. When heated with 50 per cent. sulphuric acid, or with concentrated potash, it is completely decomposed, yielding paranitraniline. If boiled for 1½ hours with alcoholic potash, or for half an hour with concentrated hydrochloric acid, it yields metanitroanthranilic acid (Hübner, *Annalen*, **195**, 21), from which different azo-dyes can be obtained.

Ethylic anthranilate hydrochloride, when mixed with concentrated potassium thiocyanate, yields a crystalline precipitate of the *thiocarbamide*, $COOEt\cdot C_6H_4\cdot NH\cdot CS\cdot NH_2$, which melts at 120—121°. If, however, the same compound is boiled for 40 hours with an excess of potassium thiocyanate solution, a white precipitate of *ketothiotetrahydroquinazoline*,  $C_6H_4{<}\begin{array}{l}CO\cdot NH\\ NH\cdot CS\end{array}$, is formed. This same compound is also obtained when the above-mentioned thiocarbamide is heated for 5 minutes at 125°.

Hübner's method (*Annalen*, **222**, 195) for the nitration of orthochlorobenzoic acid gives but poor yields, the best result being obtained by dissolving the chlorobenzoic acid (20 grams) in concentrated sulphuric acid (100 grams), and then slowly adding a mixture of 100 per cent. nitric acid (15 grams) and concentrated sulphuric acid (30 grams). Ethylic orthochlorometanitrobenzoate, melting at 28—29°, readily reacts with phenylhydrazine (4 mols.) when the mixture is warmed for several hours on the water bath, a mixture of nitrophenylindazolone and *ethylic nitrophenylhydrazidobenzoate* being formed. The latter crystallises in long, golden-yellow needles, melts at 129—130°, and is readily soluble in boiling alcohol. When hydrolysed with alkalis, it yields *nitrophenylindazolone*,  $NO_2\cdot C_6H_3{<}\begin{array}{c}CO\\ NH\end{array}{>}NPh$, which crystallises from glacial acetic acid in small, yellowish-green needles; it decomposes above 260°, and is but sparingly soluble in the usual solvents. It readily dissolves in alkalis, yielding deep red solutions; the *sodium* derivative crystallises from concentrated caustic soda solution in red plates having a green lustre. J. J. S.

Melilotol. By FRITZ WISCHO (*Chem. Centr.*, 1896, ii, 540; from *Pharm. Post.*, **29**, 309—310).—By distilling dried, flowering *Melilotus*, and shaking the distillate with ether, Phipson obtained an oily product possessing an odour like *Melilotus*, and which he named melilotol. This substance, however, is a mixture of coumarin with a little melilotaldehyde, melilotic acid, $OH\cdot C_6H_4\cdot CH_2CH_2\cdot COOH\ [=1:2]$, and its anhydride, which has an odour like that of coumarin. E. W. W.

Action of Ethylic Oxalate and Sodium Ethoxide on Nitrotoluenes. Synthesis of Nitrated Phenylpyruvic Acids. By ARNOLD REISSERT (*Ber.*, 1897, **30**, 1030—1053).—Derivatives of benzene which contain a nitro-group in the ortho- or para-position relatively to a methyl group readily condense with ethylic oxalate in presence of sodium ethoxide, yielding nitrated phenylpyruvic acids. In each case, it is necessary to find out the most suitable conditions under which the action takes place.

Orthonitrophenylpyruvic acid, $NO_2\cdot C_6H_4\cdot CH_2\cdot CO\cdot COOH$. A solution of the requisite quantities of sodium ethoxide, ethylic oxalate, and orthonitrotoluene, after being kept at 35—40° for three days, is carefully neutralised with the requisite quantity of 20 per cent. hydrochloric acid, great care being taken that the temperature does not rise. The acid and unaltered nitrotoluene are extracted with ether, and then separated by a 5 per cent. sodium hydroxide solution in which the acid is readily soluble, and can be precipitated again by hydrochloric acid in the form of an oil which slowly solidifies, and may then be recrystallised from benzene. It forms yellowish, glistening, bulky needles, sinters at 115°, melts at about 121°, and is readily soluble in hot water, in alcohol, ether, acetic acid or acetone, but only sparingly in benzene or chloroform. Solutions of the acid in caustic alkali have a deep reddish-brown colour; with alkali carbonates, the colour is not so deep. Aqueous solutions of the acid give a deep green coloration with ferric chloride. The *phenylhydrazone*,

$$NO_2\cdot C_6H_4\cdot CH_2\cdot C(COOH){:}N_2HPh,$$

forms hard, yellow, prismatic crystals, melts and decomposes at 148—149°, and is readily soluble in solutions of alkalis or alkali carbonate.

When boiled with dilute sodium hydroxide, the acid is decomposed into orthonitrotoluene, isatin, and a small quantity of *diorthodinitrodibenzyl*, which melts at 122°. Nitrous acid converts the substituted pyruvic acid into carbonic anhydride and orthonitrobenzonitrile. If less than 2 molecules of nitrous acid are used for each molecule of the acid, a small quantity of *anhydro-β-oximidorthonitrobenzoyloxalic acid*, $O[N{:}C(C_6H_4\cdot NO_2)\cdot CO\cdot COOH]_2$, is obtained as an oil; its *diphenylhydrazone* crystallises in deep yellow needles, and melts at 157°. Warm, concentrated sulphuric acid converts orthonitrophenylpyruvic acid into orthonitrophenylacetic acid, and the same product is obtained by the action of hydrogen peroxide. Potassium permanganate, both in acid and alkaline solution, yields a mixture of orthonitrobenzaldehyde and the corresponding acid. Chromic mixture yields orthonitrobenzaldehyde and orthonitrophenylacetic acid.

Orthonitrobenzylidene bromide, $NO_2\cdot C_6H_4\cdot CHBr_2$, obtained by th action of an alkaline solution of bromine on the acid, crystallises in large, colourless prisms, and melts at 46°. Bleaching powder converts the sodium salt of the nitro-acid into a compound, $C_{16}H_{12}N_2O_6$, which crystallises in long, yellowish, glistening needles, and melts at 160°. Indole-2′-carboxylic acid is obtained when orthonitrophenylpyruvic acid is reduced with zinc dust and acetic acid, but 1′-hydroxyindole-2′-carboxylic acid is formed when sodium amalgam is employed as the reducing agent. Indigo is formed when the latter acid is dissolved in concentrated sulphuric acid, the solution kept for 1—2 days at the ordinary temperature, then poured into water, and the solution saturated with ammonia and left exposed to the air in a flat dish for 1 to 2 days with constant stirring.

Paranitrophenylpyruvic acid crystallises from its acetic acid solution in hard, orange-yellow, glistening crystals, which contain 1 molecule of acetic acid; after drying, it melts at 194°. The acid is readily soluble in alcohol, ether, or acetone, and fairly readily in acetic acid, but only sparingly in water, benzene, and chloroform; its aqueous solution gives a bluish-green coloration with ferric chloride. The *phenylhydrazone* crystallises in yellow needles, and melts with decomposition at 168°.

When oxidised with chromic mixture, the acid gave a small quantity of paranitrobenzaldehyde.

Orthonitroparamethylphenylpyruvic acid is obtained from nitroparaxylene when double the quantities of sodium ethoxide and ethylic oxalate required by theory are employed; it crystallises in almost colourless needles, melts at 145°, and yields a *phenylhydrazone* melting at 170°. When reduced with zinc dust and acetic acid, it yields 2-*methylindole-2′-carboxylic acid*, which crystallises from its aqueous solution in small needles melting at 217°. When heated above its melting point, the latter acid is converted into carbonic anhydride and metamethylindole.

1′-*Hydroxy-2-methylindole-2′-carboxylic acid* is obtained when orthonitrometamethylphenylpyruvic acid is reduced with sodium amalgam; it crystallises in needles and melts at 165°.

The author has also made attempts to condense 2 molecules of ortho- or para-nitrotoluene with 1 molecule of ethylic oxalate, but the products formed were the acids already mentioned, together with small quantities of orthodinitrodibenzyl and paradinitrodibenzyl.

J. J. S.

Homologues of α-Cyanobenzoylpropionic Acid. By C. Timothée Klobb (*Bull. Soc. Chim.*, 1897, [iii], 15, 773—778).—The author has already shown that, in ethereal salts of acids of this type, the hydrogen atoms in the α-position can be replaced by sodium and subsequently by a hydrocarbon radicle, with formation of salts of the formula $COPh\cdot CH_2\cdot CR(CN)\cdot COOR'$. The paper contains an account of the action of potash on some of the ethereal salts of these acids, which have already been described.

α-Cyano-β-benzoyl-α-ethylpropionic acid, $COPh\cdot CH_2\cdot CEt(CN)\cdot COOH$, is a crystalline substance, insoluble in cold water, benzene, and chloroform, slightly soluble in hot water, and soluble in alcohol, xylene, and glacial acetic acid. It melts at 193°, and sublimes when heated. The sodium and barium salts were not obtained in the crystalline form. The silver salt crystallises from water in white crystals, which blacken when heated with water at 100°.

α-Cyano-β-benzoyl-α-methylpropionic acid is a white, crystalline substance which melts at 172°, and is very soluble in hot water, ether, alcohol, and acetic acid, slightly soluble in benzene and chloroform.

α-Cyano-β-benzoyl-α-propylpropionic acid forms white needles, soluble in water, alcohol, ether, and boiling xylene, insoluble in benzene, and melts at 189°.

α-Cyano-β-benzoyl-α-benzylpropionic acid melts at 178° and is insoluble in water, but soluble in alcohol, ether, and boiling xylene. The barium salt crystallises with $1H_2O$.

M. W. T.

Action of Phenylhydrazine on Gallic Acid and on Dibromogallic Acid. By Alexandre Biétrix (*Bull. Soc. Chim.*, 1897, [iii], 15, 783—786).—By the action of phenylhydrazine on a concentrated solution of gallic acid, two compounds are formed ; and on adding ether, crystals of the formula $C_6H_2(OH)_3\cdot CO\cdot NH\cdot NH_2Ph$ separate, which, after purification, are quite colourless, melt at 138—139°, and are very soluble in water and alcohol, but insoluble in chloroform. Its solutions give the characteristic blue with ferric chloride.

The alcohol ether solution, on standing, deposits a substance which, after recrystallisation, gives in solution no coloration with ferric chloride, indicating that no free hydroxyl groups are present. It is soluble in water, alcohol, and ether, but insoluble in chloroform. It decomposes at 185°, without melting, and from analysis has the formula $C_6H_2(NH\cdot NH_2Ph)_3\cdot CO\cdot NH\cdot NH_2Ph$.

Dibromogallic acid reacts in exactly the same way with phenylhydrazine. The monophenylhydrazine derivative, which separates on adding ether to the alcoholic solution, is soluble in water and alcohol but insoluble in ether and chloroform. It melts at 160° with decomposition, and gives the characteristic blue colour with ferric chloride. The tetraphenylhydrazide derivative resembles the corresponding derivative of gallic acid. It decomposes at 200°. M. W. T.

Norhemipinates, and the Author's Water of Crystallisation Theory. By THEODOR SALZER (*Ber.*, 1897, **30**, 1101—1104. Compare Freund and Horst, Abstr., 1894, i, 247).—Ammonium hydrogen hemipinate does not contain a molecule of water of crystallisation ; if heated, however, between 135° and 180°, it yields an anhydride by the loss of $1H_2O$. The normal ammonium salt is difficult to prepare, as the solution loses ammonia on evaporation.

The barium salt crystallises with $1H_2O$, and not with $2H_2O$; the calcium salt could only be obtained in the form of a gelatinous mass, and no definite crystals containing $3H_2O$ could be prepared. The barium hydrogen salt, $Ba(C_8H_5O_6)_2$, crystallises with $3H_2O$, which it loses at 100—125°, and between 135° and 180° it loses two more molecules of water, yielding an anhydride. The calcium hydrogen salt resembles the corresponding barium salt.

These salts form exceptions to the author's general rule.

J. J. S.

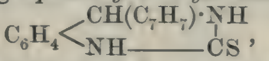
Action of Sulphurous Anhydride on Aromatic Hydroxylamines. By W. BRETSCHNEIDER (*J. pr. Chem.*, 1897, [ii], **55**, 285—304). —The hydroxylamines were prepared by reducing the corresponding nitro-compounds with zinc dust in aqueous-alcoholic solution containing a little calcium chloride (Wohl, Abstr., 1894, i, 409); it was found advisable to pass carbonic anhydride through the apparatus, and sometimes to add ether, whereby the boiling point of the mixture was lowered. The hydroxylamine was dissolved in 60 per cent. alcohol, and the solution saturated with sulphurous anhydride, being cooled meanwhile ; in many cases, where the yield of the hydroxylamine was small, this compound was never isolated, but the solution was merely filtered from the zinc, &c., and at once saturated with sulphurous anhydride.

Only phenylhydroxylamine and *paratolylhydroxylamine* (with $\frac{1}{2}H_2O$) were obtained in satisfactory amount. Most of the hydroxylamines examined give amidosulphonic acids when treated with sulphurous anhydride, the yield being best at 10°, but some sulphate of the amine is formed in addition, no doubt by the action of water on a sulphonamic acid, which might be expected to be a primary product of the action. For example, $C_6H_5\cdot NH\cdot OH$ yields $SO_3H\cdot C_6H_4\cdot NH_2$ and $C_6H_5\cdot NH_2,H_2SO_4$ (from $C_6H_5\cdot NH\cdot SO_3H$). The sulphonic group goes in the ortho-position to the amido-group; for example, phenylhydroxylamine yields 1 : 2-amidosulphonic acid, 1 : 4-tolylhydroxylamine yields 4-amido-1-methylbenzene-3-sulphonic acid, and 1 : 2-tolylhydroxylamine yields 2-amido-1-methyl-3-benzenesulphonic acid. When both ortho-positions are already occupied, as in the case of metaxylylhydroxylamine [$NHOH:Me_2 = 2:1:3$], no action takes place. In the case of 1-naphthyl hydroxylamine, 1-amido-4-naphthalenesulphonic acid is formed.

With phenylmethylhydrazine, phthalylhydroxylamine (best prepared by warming phthalimide with hydroxylamine hydrochloride and a little alcoholic ammonia), and benzhydroxamic acid, sulphurous anhydride did not form a sulphonic acid. Paratoluenesulphinic acid reacts with phenylhydroxylamine when the two substances are heated together at 100° in alcoholic solution; the product melts at 142°, and probably has the constitution $C_6H_4Me\cdot SO_2\cdot NPh\cdot OH$, for it is decomposed by aqueous alkalis into paratoluenesulphinic acid and nitrosobenzene.

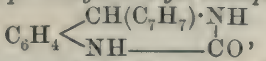
C. F. B.

Some Aromatic Amido-alcohols and their Derivatives. By HEINRICH KIPPENBERG (*Ber.*, 1897, 30, 1130—1141).—Several orthamido-alcohols were prepared by the reduction of the corresponding ketones, and it was noticed that whilst pure aromatic ketones, on treatment with sodium amalgam, yielded the alcohol, acetophenone and its derivatives were, for the most part, reduced to pinacones; thus, orthamidoacetophenone gave, on reduction, *orthodiamidoacetophenonepinacone*, $OH\cdot CMe(C_6H_4\cdot NH_2)\cdot CMe(C_6H_4\cdot NH_2)\cdot OH$, a substance crystallising from dilute alcohol, and melting at 169—170°; whilst orthamidophenyl paratolyl ketone, prepared by Hofmann's method, gave *orthamidophenylparatolylcarbinol*, $C_7H_7\cdot CH(OH)\cdot C_6H_4\cdot NH_2$, which crystallises from a mixture of benzene and light petroleum in silky, white needles melting at 99·5°; this hydrol reacts readily with thiocyanic acid, forming 4-*paratolyltetrahydrothioquinazoline*,

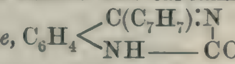


$$C_6H_4{<}\begin{matrix}CH(C_7H_7)\cdot NH\\ NH\text{———}CS\end{matrix},$$

which crystallises from alcohol in white needles melting at 224°, and with carbamide forms 4-*paratolyltetrahydroketoquinazoline*,



$$C_6H_4{<}\begin{matrix}CH(C_7H_7)\cdot NH\\ NH\text{———}CO\end{matrix},$$

crystallising in microscopic prisms melting at 208—209°. On heating a mixture of equal parts of the ketone and carbamide at 180—190°, 4-*paratolyldihydroketoquinazoline*,  $C_6H_4{<}\begin{matrix}C(C_7H_7):N\\ NH\text{——}CO\end{matrix}$, is formed; this separates from hot alcohol in greyish-yellow prisms melting at 286°.

Paramidobenzophenone, on reduction, yields *paramidobenzhydrol*, $NH_2\cdot C_6H_4\cdot CHPh\cdot OH$, which crystallises from hot water in long, white needles melting at 121°; on treatment with cold, dilute acetic acid, it gives a very insoluble compound, melting and decomposing at

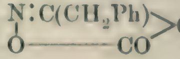
220—225°, probably *paramidobenzhydrol anhydride* $(NH \cdot C_6H_4 \cdot CHPh)_x$. On dissolving paramidobenzhydrol in dilute hydrochloric acid, and saturating the solution with hydrogen sulphide, the hydrochloride of *aa-diphenyldiparamidobenzylic sulphide*, $S(CHPh \cdot C_6H_4 \cdot NH_2,HCl)_2 + H_2O$, was produced, melting at 263°, and on treating it with dimethylaniline, water was eliminated and it was converted into *dimethyldiparamidotriphenylmethane*, $NMe_2 \cdot C_6H_4 \cdot CHPh \cdot C_6H_4 \cdot NH_2$; this melts at 117—118°. J. F. T.

Action of Aluminium Chloride on the Chlorides of Dicarbodiphenylimide. By HERBERT N. McCOY (*Ber.*, 1897, **30**, 1090—1094). —When a solution of carbodiphenylimide in benzene is saturated with hydrogen chloride, then diluted with carbon bisulphide, and digested with aluminium chloride, it is converted into a substance which has the composition and molecular weight corresponding with a dimolecular *polymeride*, $C_{26}H_{20}N_4$.

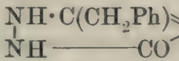
This substance exists in two forms, one of which crystallises in sulphur-yellow needles melting at 171°, whilst the second melts at 184°, and is formed when the first is heated to its melting point and then allowed to cool. Both compounds dissolve readily in dilute hydrochloric acid, forming a yellow solution, which becomes colourless on boiling. Alkalis then precipitate a white *compound*, $C_{20}H_{15}N_3O$, which crystallises in colourless needles melting at 163°, whilst aniline remains in solution. The constitution of these isomerides has not yet been determined, but it appears very improbable that they are simply symmetric polymerides. A. H.

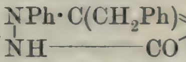
Ethylic Diphenylacetoacetate. By JAKOB VOLHARD (*Annalen*, 1897, **296**, 1—33).—Wislicenus has shown that, under the influence of sodium ethoxide, ethylic phenylacetate combines with ethylic oxalate in molecular proportion, yielding ethylic phenylacetoxalate; in attempting to induce the combination of ethylic phenylacetate with two molecular proportions of ethylic oxalate, the author has obtained ethylic diphenylacetoacetate, $CH_2Ph \cdot CO \cdot CHPh \cdot COOEt$, which is formed by the elimination of ethylic alcohol from two molecular proportions of the ethereal salt.

Ethylic diphenylacetoacetate, $CH_2Ph \cdot CO \cdot CHPh \cdot COOEt$, is prepared by agitating ethylic phenylacetate (65 parts) with sodium ethoxide (27·5 parts) which has been prepared from anhydrous alcohol and dried in hydrogen at 200°; the liquid is then heated on the water bath for half an hour after the sodium ethoxide has dissolved, rapidly cooled, and the solid product dissolved in water and acidified with acetic acid. The salt crystallises from alcohol in lustrous, colourless needles, and melts at 78—79°; it is insoluble in water, but dissolves readily in the usual organic solvents. Prolonged treatment with a boiling solution of barium hydroxide converts it into phenylacetic acid; an alcoholic solution yields the blue, crystalline, *copper* derivative when treated with copper acetate. The *oxime* separates from alcohol in compact, colourless crystals, and melts at 112—113°; when dissolved in concentrated sulphuric acid, it undergoes partial conversion into phenylbenzylisoxazolone.

Phenylbenzylisoxazolone,  $\begin{matrix} N:C(CH_2Ph) \\ | \qquad\qquad \\ O\text{———}CO \end{matrix}\!\!>\!CHPh$, produced along with

the oxime when hydroxylamine acts on ethylic diphenylacetoacetate, crystallises in lustrous needles melting at 106—107°; the *silver* derivative is crystalline, and the *aniline*, *toluidine*, and *phenylhydrazine* salts melt at 112—113°, 116—118°, and 118—119° respectively. An alcoholic solution of phenylbenzylisoxazolone develops an intense green coloration with ferric chloride, the *compound*, $C_{32}H_{24}N_2O_5$, which crystallises in colourless, six-sided plates, and melts at 148—149°, being also produced; this substance, unlike phenylbenzylisoxazolone, is quite insoluble in alkalis.

Phenylbenzylpyrazolone,  $\begin{matrix}\mathrm{NH\cdot C(CH_2Ph)} \\ | \\ \mathrm{NH}\text{———}\mathrm{CO}\end{matrix}\!>\mathrm{CPh}$, arises from the action of hydrazine hydrate on ethylic diphenylacetoacetate, and crystallises from alcohol in tufts of slender needles containing 1 mol. of the solvent. After the first crystallisation, the melting point is 125—126°, but is raised to 141° by recrystallisation from toluene, and if the substance is again crystallised from alcohol, it melts at 172°. The *methyl* derivative crystallises from methylic alcohol, in which it is sparingly soluble, and melts at 237—238°.

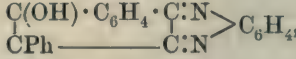
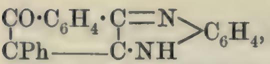
Diphenylbenzylpyrazolone,  $\begin{matrix}\mathrm{NPh\cdot C(CH_2Ph)} \\ | \\ \mathrm{NH}\text{———}\mathrm{CO}\end{matrix}\!>\mathrm{CPh}$, prepared by heating ethylic diphenylacetoacetate with phenylhydrazine in glacial acetic acid, crystallises from much hot alcohol in slender, white needles. It dissolves more readily in glacial acetic acid, and melts at 231—232°. The *methyl* derivative crystallises from alcohol.

Concentrated sulphuric acid eliminates alcohol from ethylic diphenylacetate, converting it into a derivative of naphthalene; this change is analogous to the production of naphthol or its derivatives from phenylisocrotonic, phenylparaconic, or benzylidenelevulinic acid. The exact nature of the naphthalene derivative must, for the present, remain undecided, as some of its properties appear to be consistent with a ketonic structure, whilst in other respects it is hydroxylic in character; oxidation converts it into a quinhydrone, which then passes into a hydroxyquinone. The latter, when distilled with zinc dust, yields β-phenylnaphthalene.

1 : 3 : 2-*Dihydroxyphenylnaphthalene* is obtained by dissolving ethylic diphenylacetoacetate in 10 parts of concentrated sulphuric acid; it crystallises from chloroform in colourless, six- or eight-sided plates, and melts at 165—166°. It becomes pink when exposed to the air, and ferric chloride develops a deep red coloration. The *diacetyl* derivative separates from alcohol in lustrous, white, prismatic crystals, and melts at 136—137·5°.

1 : 2-*Hydroxyphenyl-β-naphthaquinone*, or 3 : 2-*hydroxyphenyl-α-naphthaquinone*, is prepared by passing air for 24 hours through a solution of 1 : 3 : 2-dihydroxyphenylnaphthalene in caustic soda; it crystallises from alcohol in long, yellow needles, and melts at 146—147°. It dissolves readily in ammonia, alkalis, and alkali carbonates, forming reddish-brown solutions; concentrated sulphuric acid dissolves it with a brownish coloration, becoming green, and finally intensely blue when the solution is agitated with benzene containing thiophen. The *silver* derivative, which is crystalline, and brownish-red, dissolves readily in alcohol and water; the *methyl* ether separates from methylic alcohol

in compact, brownish-yellow crystals, and melts at 122—123°. The *acetate* melts at 112—113·5°, and the *phenylhydrazone* crystallises from alcohol in prismatic needles, and melts, decomposing, at 200°; the *hydrazone* is brownish-yellow and crystalline, and the *oxime* separates from alcohol in yellow needles melting at 215—216°, when it decomposes. Both the oxime and phenylhydrazone develop intense coloration with ferric chloride.

Phenylhydroxynaphthaphenazine,  $\begin{matrix}C(OH)\cdot C_6H_4\cdot C{:}N \\ CPh\text{——————}C{:}N\end{matrix}>C_6H_4$, or  $\begin{matrix}CO\cdot C_6H_4\cdot C{=}N \\ CPh\text{———}C\cdot NH\end{matrix}>C_6H_4$, obtained by heating the hydroxyquinone with alcoholic orthophenylenediamine, crystallises from chloroform in reddish-violet needles melting at 229—231°; the *sodium* derivative crystallises in beautiful, long, red needles, exhibiting greenish, metallic surface lustre, and the *silver* derivative is violet. The *acetyl* derivative crystallises in lustrous, yellowish needles, and melts at 262—262·5°.

Phenylhydroxynaphthaquinhydrone, $C_{16}H_{11}O_2\cdot O\cdot C_{16}H_{11}O_2$, is the intermediate product in the conversion of the hydroxynaphthol into the hydroxyquinone, and separates from the mother liquor on adding light petroleum to it; it is more conveniently prepared, however, by passing air for 12—14 hours through a solution of the hydroxynaphthol in alcoholic ammonia, and is thus obtained in lustrous, red crystals melting at 171·5—172·5°. The *silver* derivative is bluish-red.

The *compound*, $C_{32}H_{20}O_6$, is obtained on oxidising hydroxyphenylnaphthaquinone in alcoholic solution with ferric chloride; it dissolves sparingly in alcohol and glacial acetic acid, but crystallises from aniline or nitrobenzene in reddish-brown needles, and melts at 278—280°. M. O. F.

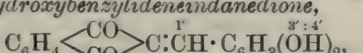
Oxidation of the Rosanilines by Lead Dioxide. By MAURICE PRUD'HOMME (*Bull. Soc. Chim.*, 1897, iii, 15, 780—783).—The author contradicts Rosenstiel's statement (this vol., i, 225) that the colour of the rosaniline bases precipitated from solution by alkalis is due to the adherence of some of the salt.

The changes which 'patent blue' or metahydroxy-malachite green undergoes when oxidised are compared with those which take place on oxidation of other rosaniline dyes. When oxidised in acid solution by lead dioxide, 'patent blue' appears to be the only member of the class which does not give an alkylated benzidine; on adding lead peroxide and acetic acid to the precipitated base, however, it appears to behave in the usual manner. M. W. T.

Flavone Derivatives. V. Ketocumaran and some of its Condensation Products. By PAUL FRIEDLÄNDER and JULIUS NEUDÖRFER (*Ber.*, 1897, 30, 1077—1083).—Orthohydroxyacetophenone, which is best prepared from nitrophenylacetylene, readily yields the acetate when it is heated at 150° with acetic anhydride. The acetate is converted by bromination in solution in carbon disulphide into *acetoxyacetophenone bromide*, $OAc\cdot C_6H_4\cdot CO\cdot CH_2Br$, which crystallises in long, white needles melting at 67°. When the latter is boiled with chalk and water, it is converted into *ketocumaran*, $C_6H_4<\substack{O\\CO}>CH_2$, which crystallises in white needles, melts at 97°, and dissolves in aqueous soda but is reprecipitated by acids; when the alkaline solution is warmed, decomposition occurs and salicylaldehyde is produced. On treatment with alkaline oxidising agents, such as Fehling's solution, it is converted into a blue compound, which will form the subject of a separate communication. Ketocumaran and orthohydroxyacetophenone bromide readily react with aldehydes to form flavone derivatives. *Flavone*, $C_{15}H_{10}O_2$, is formed by the condensation of ketocumaran with benzaldehyde, and separates in almost colourless crystals melting at 108°; it gives an orange-yellow coloration with sulphuric acid, and is insoluble in aqueous soda in the cold, but is decomposed on heating. *Dihydroxyflavone*, $C_{15}H_{10}O_4$, obtained when protocatechuic aldehyde is employed, forms brownish-yellow needles melting at 224°; it gives a bluish-violet coloration with concentrated aqueous soda, and an orange coloration with sulphuric acid. The *acetate* melts at 134°. *Methylenedihydroxyflavone*, $C_{16}H_{10}O_4$, is prepared from piperonal, and forms deep yellow needles melting at 192°. It is insoluble in alkalis, and gives an eosin red coloration with sulphuric acid.

A comparison of the different flavone derivatives shows that the position of the hydroxyl groups has a great influence on the colorations which they yield with sulphuric acid and with aqueous soda. A. H.

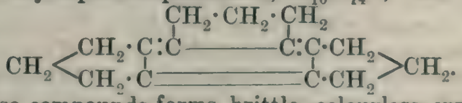
3′ : 4′-Dihydroxybenzylideneindanedione. By Stanislaus von Kostanecki (*Ber.*, 1897, **30**, 1183—1186. Compare Abstr., 1896, i, 606).—3′ : 4′-*Dihydroxybenzylideneindanedione*,



$$C_6H_4<\substack{CO\\CO}>C{:}\overset{1'}{C}H\cdot C_6H_3(\overset{3':4'}{OH})_2,$$

prepared by heating protocatechuic aldehyde with indanedione in molecular proportion at 110—120°, and crystallises from alcohol in brownish-yellow needles; it sublimes in small, yellow needles, and melts and decomposes at 257°. The solution in alkalis is reddish-violet, finally becoming brownish-yellow; with alum mordants, it behaves as a yellow colouring matter. The *diacetyl* derivative crystallises in yellowish prisms, and melts at 186°. The *methylenic ether* is prepared from indanedione and piperonaldehyde; it crystallises from pyridine in magnificent, intensely yellow needles, and melts at 209°. The *monomethylic ether*, obtained from indanedione and vanillin, crystallises in long, yellow needles melting at 212°; the *acetyl* derivative of the monomethyl ether melts at 184—185°. M. O. F.

Condensation Products of Cyclic Ketones III. By Otto Wallach (*Ber.*, 1897, **30**, 1094—1096. Compare Abstr., this vol., i, 159).—When cyclopentanone is saturated with hydrogen chloride and allowed to remain for several weeks, it yields, on distillation, unaltered cyclopentanone, dicyclopentenepentanone, $C_{10}H_{14}O$, and *tricyclotrimethylenebenzene*,



The last of these compounds forms brittle, colourless crystals melting at 96—97°, and is not attacked by dilute potassium permanganate, but is readily oxidised by dilute nitric acid and by chromic acid. It has a molecular weight corresponding with the above formula, and is apparently formed from the pentanone in the same way as mesitylene from acetone. A. H.

Naphthalene Tetrabromide. By William R. Orndorff and C. B. Moyer (*Amer. Chem. J.*, 1897, 19, 262—270).—*Naphthalene tetrabromide* may be prepared by the gradual addition of bromine to well-cooled naphthalene mixed with a small quantity of sodium hydroxide. The deep red, pasty mass was purified by repeated treatment with small quantities of lukewarm alcohol, which extracted unchanged naphthalene, α-monobromonaphthalene, and 1 : 4-dibromonaphthalene; the residue was recrystallised several times from chloroform, when transparent, monoclinic prisms were obtained, which became opaque on exposure to light, or when heated. The crystals melt and decompose at 111°, are insoluble in water, ether, glacial acetic acid, and cold alcohol, but readily soluble in carbon bisulphide, light petroleum, hot chloroform, and benzene.

The yield was very small, but although the process was modified in various ways, it could not be improved, nor could any other tetrabromide be isolated.

Attempts to separate a stereoisomeride from this tetrabromide proved unsuccessful.

When heated to several degrees above its melting point, bromine and hydrogen bromide are given off, 1 : 4-dibromonaphthalene and a monobromonaphthalene being formed. On boiling with alcoholic potassium hydroxide, it is completely decomposed, the product consisting mainly of a bromonaphthalene. On oxidation with nitric acid, the only product identified was phthalic acid.

Attempts to determine the molecular weight of the tetrabromide by the boiling point method proved unsuccessful owing to decomposition, even when substances with such low boiling points as chloroform and carbon bisulphide were used. A. W. C.

Derivatives of Dihydroxynaphthalene. By Rudolf Nietzki and Th. Knapp (*Ber.*, 1897, 30, 1119—1124. Compare Clausius, Abstr., 1890, 627).—2′ : 1 : 2-*Hydroxynaphthaquinonedioxime*,

$$OH\cdot C_{10}H_5(N\cdot OH)_2,$$

obtained when an alcoholic solution of the monoxime described by Clausius is boiled with hydroxylamine hydrochloride, crystallises from dilute acetic acid in light, orange-coloured needles, melts at 195°, and is readily soluble in alcohol, ether, ethylic acetate, and acetic acid. The dioxime readily yields an internal anhydride; on warming with concentrated potash, crystals of the *potassium* salt of this anhydride are formed. On decomposing the potassium salt with hydrochloric acid, the anhydride, *β-naphtholfurazan*, is obtained; this crystallises from alcohol in long, colourless needles melting at 213—214°. If the dioxime is warmed with acetic anhydride, the *acetyl* derivative of β-naphtholfurazan is obtained; this forms silky needles, melts at 137°, and on hydrolysis yields the furazan. *Trinitrodinitroso-β-naphthol*, obtained by the action of nitric acid (sp. gr. 1·4) on a mixture of the dioxime and glacial acetic acid, forms a sparingly soluble *potassium* salt, crystallising in orange-yellow plates, and exploding when heated to 260°. To prepare the pure free naphthol, the potassium salt is dissolved in fuming nitric acid and water added; it forms glistening, rhombic, yellow crystals, melts at 208°, and explodes at a slightly higher temperature. Its *ethylic* ether crystallises in pale yellow needles, melts at 167°, and is readily soluble in benzene.

Dinitrodinitroso-β-naphthol, obtained by the action of nitric acid on the dioxime and glacial acetic acid in the cold, crystallises in yellow needles, and melts at 196°; its *potassium* salt crystallises in small, red needles, and is moderately soluble in water.

Trinitro-β-naphtholfurazan is obtained when the acetyl derivative of β-naphtholfurazan is nitrated with fuming nitric acid. It crystallises from toluene in orange-coloured, glistening needles, which contain toluene of crystallisation. It is readily soluble in alkalis, and forms a sparingly soluble *barium* salt.

When amidodihydroxynaphthalene, obtained by the reduction of nitrosodihydroxynaphthalene (Clausius, *loc. cit.*), is warmed with anhydrous sodium acetate and acetic anhydride, it yields a *triacetyl* derivative melting at 183°, but if the heating is continued, a *tetracetyl* derivative, $C_{10}H_5(OAc)_2\cdot NAc_2\,[=2':2:1]$, which melts at 135°, is formed. The authors find that Clausius' 1 : 2 : 2′-hydroxynaphthaquinone crystallises in brown needles and melts at 194°. When the dioxime described above is carefully reduced with stannous chloride and hydrochloric acid, diamido-β-naphthol hydrochloride $[(NH_2)_2 : OH = 1 : 2 : 2']$ is obtained; it yields a *triacetyl* derivative melting at 244—245°.

J. J. S.

Derivatives of Anthracene and of Anthraquinone. By CARL GRAEBE and SIEGFRIED BLUMENFELD (*Ber.*, 1897, **30**, 1115—1119. Compare Graebe and Leonhardt, Abstr., 1896, i, 437).—*Methylic anthraquinone-1-carboxylate* forms pale yellow crystals and melts at 189°. The *amide* of anthraquinone-1-carboxylic acid, obtained by passing dry ammonia into a benzene solution of the chloride, crystallises from alcohol and melts at 280°. 1-*Amidoanthraquinone* was obtained by the action of bromine and potash on the amide, and is identical with the compound described by Römer, but has not the properties ascribed to it by Böttger and Petersen. The acetyl derivative of the base melts at 215° (corr.) and not at 202°, as stated by Römer. 1-Nitroanthraquinone melts at 228° (corr.); Böttger and Petersen give 230°, and Römer gives 220°.

Anthraquinone-1-carboxylic acid, when reduced with zinc dust and ammonia, yields an anthracene-1-carboxylic acid melting at 245°; this is probably identical with the acid described by Liebermann and Rath (*Ber.*, 1875, **8**, 246) as melting at about 260°. The *amide* melts at 260°, and crystallises in pale yellow plates; it is not readily decomposed when heated with dilute soda. J. J. S.

Terpenes and Ethereal Oils. By OTTO WALLACH (*Annalen*, 1897, **296**, 120—133. Compare Abstr., 1894, i, 337).—Attention has been drawn (*loc. cit.*) to the resemblance between menthonitrile and its derivatives, and certain compounds of the citronellic series; it is now shown that, through the nitrile, menthone is convertible into open chain compounds, a process which gains interest from the fact that the converse change, namely, production of pulegone from citronellaldehyde, has been accomplished recently (Tiemann and Schmidt, this vol., i, 198).

Menthonenic (decenoic) *acid*, $C_9H_{17}\cdot COOH$, is produced on hydrolysing menthonitrile with sodium ethoxide in sealed tubes at 120°; it boils at 257—261°, has the sp. gr. $= 0\cdot918$, and the refractive index $n_D = 1\cdot45109$ at 20°. Oxidation with potassium permanganate gives rise to β-methyladipic acid, the substance which Tiemann and Schmidt obtained from citronellic acid by the same process (Abstr., 1896, i, 383); in spite of the resemblance between citronellic and menthonenic acids, however, close comparison shows that they are not identical, this being probably due to the different situation of the ethylenic linking.

A *decoic acid*, $CHMe_2\cdot CH_2\cdot CH_2\cdot CH_2\cdot CHMe\cdot CH_2\cdot COOH$, is prepared by heating menthoneoxime (10 grams) with caustic potash (10 grams) and water (2 c.c.) at 220—230° for an hour, and boils at 249—251°; it has the sp. gr. $= 0\cdot905$, and the refractive index $n_D = 1\cdot4373$. The *amide* crystallises from water, and melts at 108—109°.

When menthonitrile is reduced, two bases are obtained, menthonylamine, $C_{10}H_{19}NH_2$, and hydroxyhydromenthonylamine, $OH\cdot C_{10}H_{20}\cdot NH_2$, which is not volatile in steam (Abstr., 1894, i, 338); the alcohol produced by the action of nitrous acid on the former base is called *menthocitronellol* by the author, and has the constitution

$$CMe_2{:}CH\cdot CH_2\cdot CH_2\cdot CHMe\cdot CH_2\cdot CH_2\cdot OH,$$

ascribed by Tiemann and Schmidt to natural citronellol (Abstr., 1896, i, 383). *Dimethyloctylene glycol* (2 : 6-*dimethyloctane*-2 : 8-*diol*),

$$OH\cdot CMe_2\cdot CH_2\cdot CH_2\cdot CH_2\cdot CHMe\cdot CH_2\cdot CH_2\cdot OH,$$

is obtained in the same way from hydroxyhydromenthonylamine, and boils at 153—156° under a pressure of 19 mm.; dilute sulphuric acid converts it into menthocitronellol.

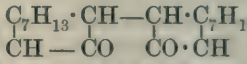
Menthocitronellaldehyde, $C_9H_{17}\cdot COH$, prepared by oxidising the alcohol with chromic acid, boils at 86—88° under a pressure of 16 mm. and at about 200° under atmospheric pressure; it has the sp. gr. $= 0\cdot8455$, and the refractive index $n_D = 1\cdot43903$ at 20°. The citronellal-β-naphthocinchonic acid obtained by condensation with β-naphthylamine and pyruvic acid melts at 214—215°, and is therefore different from the compound with natural citronellaldehyde, which melts at 225° (Doebner, Abstr., 1894, i, 261). The semicarbazone is optically inactive, and melts at 89° (compare Tiemann and Schmidt, this vol., i, 199). M. O. F.

Oil of Levisticum officinale. By R. Braun (*Arch. Pharm.*, 1897, **235**, 1—19).—Oil of lovage has the characteristic taste and odour of Levisticum root. Its sp. gr. varies somewhat, the mean value $= 1\cdot0407$ at 15°, and its refractive index $= 1\cdot5336$—$1\cdot5337$. It is readily soluble in alcohol (96 per cent.), ether, light petroleum, chloroform, acetic acid, &c. Iodine has no action, but bromine converts the oil into a resinous mass; potassium also acts violently, and on the addition of water an orange-red emulsion is obtained. When warmed with platinic chloride, an odour of angelic acid is developed. The oil begins to boil at about 170°, but at 200° decomposition ensues; it was therefore distilled under diminished pressure, and the following fractions collected: (1) to 130°; (2) 130—176°, mostly 170—176°; (3) 200—250°, coloured brown; (4) 250—300°, coloured green; (5) 300—360°, dark green. These temperatures are calculated to normal pressure. Fraction 5 solidified on cooling, and was found to contain benzoic acid. Fractions 1, 3, and 4 were very small, and could not be investigated. Fraction 2 was found to contain two compounds. One of these, $C_{10}H_{18}O$, boils at 178°, has a sp. gr. $=0{\cdot}9176$ at 15°, and a refractive index $= 1{\cdot}4825$; in its physical properties, it resembles cineol, but does not yield crystalline additive compounds with hydrogen chloride or with bromine. The second compound, $C_{10}H_{16}$, is best obtained by the prolonged action of alcoholic potash (30 per cent.) on the compound, $C_{10}H_{18}O$. It is a clear, colourless oil, with an odour resembling that of thyme; it boils at 176°, has a sp. gr. $=0{\cdot}8534$ at 15°, and a refractive index $=1{\cdot}4777$; it is dextrorotary $(+5°)$, and in many respects resembles limonene, but yields no crystalline additive compound with bromine. A resinous substance was also obtained by the action of alcoholic potash on the compound $C_{10}H_{18}O$. When fused with potash, acetic, isovaleric, and benzoic acids were found among the products formed.

The oil from fresh roots appears to differ in some of its physical constants from the oil from the dried roots. The green roots also, on distillation, yield little or no resin. J. J. S.

French Oil of Basil. By JUSTIN DUPONT and JACQUES GUERLAIN (*Compt. rend.*, 1897, **124**, 300—302).—This oil, obtained by distilling the leaves of *Ocymum basilicum* with water, has a yellowish colour and a strong characteristic smell. It has a sp. gr. $=0{\cdot}9154$ at 15°, and a rotation of $-7°\ 40'$ in a 100 mm. tube. When distilled under atmospheric pressure, four-fifths pass over between 190—220°, a brown resinous mass remaining in the distilling flask, and on further fractionation, two main fractions are obtained, the one boiling at 195—200°, the other at 205—215°. The former is an oily, refractive liquid possessing the odour of lævorotatory linalol, and having the formula $C_{10}H_{18}O$; the following properties are recorded: sp. gr. $= 0{\cdot}8552$ at 15°; $[\alpha]_D = -14{\cdot}03°$; index of refraction, $n_D = 1{\cdot}4565$; molecular refraction = 49. It combines with 4 atoms of bromine, giving an uncrystallisable liquid product, and, on heating with acetic anhydride, an *acetate* boiling at 128° (14 mm.), which, on saponification with alcoholic potash, yields geraniol, boiling at 115—117° (15 mm.). This fraction, therefore, consists of lævorotatory *linalol*. The fraction boiling at 205—215° had the odour of estragol, and exhibited a rotation of $-6°\ 40'$ in a 100 mm. tube. Even after treatment with alcoholic potash, in order to free it from ethers, and further fractionation, it was found impossible to obtain a product of definite composition. Its odour, its boiling point, and the formation of methylic iodide on treatment with hydriodic acid, having rendered it probable that this fraction consisted chiefly of estragol, it was heated with concentrated alcoholic potash for 24 hours, and after treatment with water and extraction with ether, the product was fractionally distilled. The main fraction, boiling at 225—230°, instantly solidified on the addition of a crystal of anethol, and melted, after drying between filter paper, at 21°. The second fraction, therefore, of the oil consisted of *estragol* (paramethoxyallylbenzene). A. C. C.

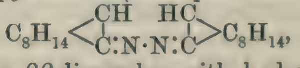
ββ-Dicamphor. By GIUSEPPE ODDO (*Gazzetta*, 1897, **27**, i, 149—194. Compare Abstr., 1894, i, 201).—On heating bromocamphor with sodium and toluene in a reflux apparatus on an oil bath, reduction occurs suddenly; after heating for 5 hours, water is added, and the toluene and aqueous solutions are distilled separately in a current of steam. Toluene, borneol, and camphor distil from the toluene solution, leaving a crystalline mass, which, on recrystallisation from alcohol and a mixture of petroleum and benzene, yields dicamphanhexane-1 : 4-dione, whilst the aqueous solution remaining in the distilling flask, when evaporated to dryness and crystallised from acetic acid, yields ββ-dicamphor. The original aqueous washings, after being freed from volatile products by a current of steam, diluted, and acidified, yield a mixture of α-camphandioic anhydride, β-*trans*-dicamphandioic acid, and camphanonedicamphanonic acid, which are separated by treatment with soda and acid and crystallisation from alcohol.

I.—*ββ-Dicamphan*-1 : 4-*dione* (ββ-dicamphor), 

$$\begin{array}{llll} C_7H_{13}\cdot & CH & — CH & \cdot C_7H_{13} \\ \quad | & \ | & \ \ | & \quad | \\ CH & — CO & \ \ CO & \cdot CH \end{array},$$

can also be prepared by reducing dicamphanhexane-1 : 4-dione or dicamphenehexadiene peroxide with zinc dust and acetic acid in alcoholic solution; it crystallises in colourless prisms melting at 165—166°, has the normal molecular weight in freezing benzene, and was previously termed dicamphoryl (Abstr., 1894, i, 202). In a 5 per cent. benzene solution at 27°, it has a specific rotation of $[\alpha]_D = -28·4°$, whilst in a 25 per cent. absolute alcoholic solution at 22°, $[\alpha]_D = -4·69°$; it is odourless, boils and decomposes at above 350°, and reacts with fuming hydrochloric acid at 150°. The *phenylhydrazone*, $C_{26}H_{36}N_2O$, crystallises in lustrous, white scales melting at 142—145°, and readily undergoes hydrolysis.

Dicamphandihydropyridazine (dicamphanazine),

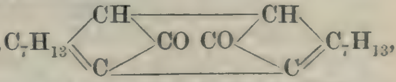


$$C_8H_{14}\left\langle\begin{array}{l} CH \quad\ HC \\ \ | \qquad\quad\ \ | \\ C{:}N\cdot N{:}C \end{array}\right\rangle C_8H_{14},$$

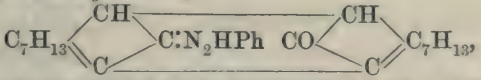
is prepared by boiling ββ-dicamphor with hydrazine hydrochloride in acetic acid solution; it crystallises in colourless, lustrous scales melting at 155—156°, has the normal molecular weight in freezing benzene, and in a 5 per cent. benzene solution at 22° has a specific rotation of $[\alpha]_D = +118·8°$. The *hydrochloride*, $C_{20}H_{30}N_2,HCl$, crystallises in white needles which do not melt at 265°, and the *picrate*, $C_{20}H_{30}N_2,C_6H_3N_3O_7$, in yellow needles which decompose at 200—205°; it is hydrolysed by boiling water. The *methiodide*, $C_{20}H_{30}N_2,MeI$, is prepared by heating the base with methylic iodide, and crystallises in white, prismatic needles melting at 207—208°. A *substance* crystallising in lustrous, white scales melting at 146—147° is also obtained in the preparation of dicamphanazine.

By the reduction of dicamphenehexadiene peroxide with zinc and acetic acid, a mixture of ββ-dicamphor and *isodicamphor* is obtained; the latter could not be satisfactorily purified, and melts at 90—95°. It contains only one oxygen atom replaceable by hydrazine with formation of a *base*, $C_{10}H_{15}O\cdot C_{10}H_{15}\cdot N_2H_2$, which crystallises in lustrous, white scales melting at 165—166°; it is readily hydrolysed by hot hydrochloric acid, and shows very feeble reducing properties towards Fehling and alcoholic silver nitrate solutions.

II.—*Dicamphanhexane*-1:4 *dione*,

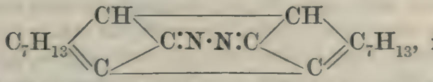


is prepared by fusing $\beta\beta$-dicamphor with caustic potash at 200°, extracting the product with water, and crystallising the residue; it is also obtained during the treatment of bromocamphor with sodium, as described above. It crystallises in beautiful, yellow needles or plates melting at 192—193°, has the normal molecular weight in freezing benzene, and is very soluble in organic solvents; its specific rotation in a 3·5 per cent. benzene solution at 27° is $[\alpha]_D = +331°$, and in a 2·9 per cent. absolute alcoholic solution at 24°, $[\alpha]_D = +381°$. It distils at 332—335°, being completely converted into the isomeric dicamphenehexadiene peroxide; the same change occurs, although less completely, on heating with acetic anhydride or hydrochloric acid at 200—230°. Its *monhydrazone*,



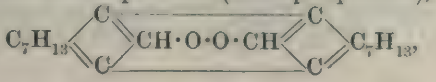
crystallises in lustrous, red scales melting at 117—118°; when dissolved in hot, dilute sulphuric acid, repeatedly crystallised from alcohol, or by prolonged boiling with water, it is converted into *isodicamphor-1-one-4-hydrazone*, $C_{20}H_{34}N_2O$, which crystallises in small, yellow needles melting at 177—178°.

Dicamphanhexaneazine,

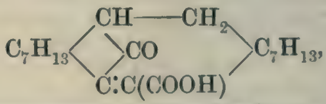


is obtained in theoretical yield on boiling the dione with hydrazine hydrochloride in acetic acid solution; it crystallises in lustrous, white scales melting at 201—202°, has the normal molecular weight in freezing benzene, and has a specific rotation of $[\alpha]_D = +52·6°$ in a 5 per cent. benzene solution at 27°. It has a bitter taste and is physiologically very active. Its *hydrochloride*, $C_{20}H_{28}N_2,HCl$, crystallises in white needles melting at 230—235°, and its *picrate*, $C_{20}H_{28}N_2,C_6H_3N_3O_7$, in small, yellow prisms melting at 237° with decomposition; the *aurochloride*, $C_{20}H_{28}N_2,HAuCl_4$, crystallises in beautiful, yellow prisms melting and decomposing at 195—199°, and the *platinochloride*, $C_{20}H_{28}N_2,HCl,PtCl_4$, crystallises in red prisms decomposing at 260°. The *methiodide*, $C_{20}H_{28}N_2,MeI$, crystallises in beautiful, white needles melting at 201—202°; when treated with moist silver oxide in aqueous solution, it yields *dicamphanhexaneazinemethylammonium hydroxide*, $C_{20}H_{28}N_2,MeOH$, which crystallises in deliquescent, white needles and is a powerful base. Its *aurochloride*, $C_{20}H_{28}N_2,MeAuCl_4$, crystallises in scales melting at 200—202°, its *chloride*, $C_{20}H_{28}N_2,MeCl$, in white needles melting at 170° with decomposition, whilst its *nitrate* separates from water in small, white crystals which decompose at 210°.

Dicamphenehexadiene peroxide (dicamphoquinone),

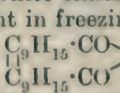


may be prepared by the methods indicated above, or by treating the mixture obtained by the action of sodium on bromocamphor first with carbonic anhydride and then with water; it crystallises in beautiful, yellow scales melting at 155—156°. It has a specific rotation of $[\alpha]_D = +296{\cdot}2°$ in a 3·5 per cent. benzene solution at 16° and of $[\alpha]_D = +345{\cdot}3°$ in a 2·9 per cent. absolute alcohol solution at 15°; it is noteworthy that the difference between the specific rotations in benzene and alcohol is the same for both the peroxide and the isomeric dione. The latter does not combine with bromine, whilst the peroxide readily takes up 4 atoms of bromine giving an unstable product, but it does not react with phenylhydrazine or hydroxylamine, and only gives traces of dicamphanhexaneazine with hydrazine hydrochloride. The peroxide is not acted on by acetic anhydride or phenylcarbimide at 220—230°, although partial decomposition occurs; it is reduced by zinc and acetic acid to a mixture of ββ-dicamphor and isodicamphor, and is converted into the isomeric dione by treatment with sodium in toluene solution.



III.—*Camphanonecamphanonic acid*, crystallises in colourless, transparent, monosymmetric plates [$a:b:c = 0{\cdot}9407:1:0{\cdot}6065.\ \beta = 87°\ 11'$] melting at 224—225°; it has the normal molecular weight in freezing acetic acid, but in benzene solutions approximately double the normal values are obtained. In a 4·7 per cent. absolute alcohol solution at 12·6°, it has a specific rotation of $[\alpha]_D = +98{\cdot}36°$. Its *silver* salt, $AgC_{20}H_{29}O_3$, is obtained as a flocculent, white precipitate readily altered by light, the *methylic* salt crystallises in lustrous, white needles melting at 94—95°, and the *ethylic* salt in white needles melting at 79°. The acid does not combine with bromine in acetic acid solution.

β-trans-Camphandioic acid, $COOH\cdot C_9H_{15}\colon C_9H_{15}\cdot COOH$, is obtained in colourless, transparent, hemihedral, monosymmetric crystals melting at 265—266°; it has rather less than the normal molecular weight in freezing acetic acid, and in a 2·25 per cent. absolute alcohol solution at 18·5° has a specific rotation of $[\alpha]_D = +90{\cdot}6°$. The triacid *potassium* salt, $C_{20}H_{32}O_4, C_{20}H_{31}KO_4$, crystallises in microscopic prisms and is sparingly soluble in boiling water; the *silver* salt, $C_{20}H_{30}Ag_2O_4$, was also prepared. On heating the acid with acetic chloride at 120—130° for 2 hours, it yields *β-cis-camphandioic anhydride* $(C_{10}H_{15}O)_2O$ which is white and crystalline and melts at 162°; when treated with soda and then with hydrochloric acid, it gives *β-cis-camphandioic acid*, which crystallises in lustrous, white scales melting at 176—180° and has the normal molecular weight in freezing acetic acid.



α-Dicamphandioic anhydride, $\left.\begin{matrix}C_9H_{15}\cdot CO\\ | \\ C_9H_{15}\cdot CO\end{matrix}\right>O$, crystallises in lustrous, white scales melting at 143—144°, gives the normal molecular weight in benzene and acetic acid by the cryoscopic method, and has a specific rotation of $[\alpha]_D = -142°$ in a 1·1 per cent. alcoholic solution at 14°. It separates unchanged on acidifying its solution in alkalis. The *silver* salt, $C_{20}H_{30}Ag_2O_4, H_2O$, of the corresponding acid was prepared.

W. J. P.

Coronilla and Coronillin. By C. Frederic Schlagdenhauffen and E. Reeb (*Chem. Centr.*, 1896, ii, 430—431; from *Zeit. Österr. Apoth.-V.*, **34**, 487—490, 507—510, 527—532).—The authors have examined the seeds of *Coronilla scorpioides* botanically and chemically. From the powdered seeds, about 4·3 per cent. of an orange-yellow, fatty oil of sp. gr. 0·912, was extracted by means of light petroleum. This oil, which becomes brown by the action of sulphuric acid and with ferric chloride turns violet, contains cholesterol and lecithin and on saponification yields oleic, arachic, stearic, and palmitic acids.

Coronillin is obtained by digesting the powdered seed, deprived of oil, with six times its weight of water at 100°, then adding an equal quantity of 95 per cent. alcohol, and after three days filtering and evaporating to one-sixth its weight. In about 24 hours, crystals of *pseudocoumarin*, $C_7H_4O_2$, separate, which on heating emit a coumarin-like odour. The filtrate from the crystals is evaporated to the consistency of the extract, the filtrate treated with 95 per cent. alcohol (for 50 grams extract 3 litres alcohol), the solution filtered, the alcohol distilled off, and the residue dissolved in water and shaken with ether. When the aqueous solution, after adding sodium sulphate and magnesium sulphate, is evaporated to 100 grams on the water bath, a thick mass separates; this is dissolved in alcohol, filtered, the filtrate treated with lead acetate, and the lead removed by hydrogen sulphide, the filtrate from this being evaporated to dryness, again dissolved in water, filtered through porcelain and again evaporated. The residue, after washing with boiling chloroform and ether and dissolving in a little alcohol, is finally treated with ether and the yellowish filtrate evaporated. The amber-coloured residue of coronillin is easily soluble in water, alcohol, and acetone, but only very slightly in ether and chloroform. It is a glucoside and is easily decomposed by dilute acids: $2C_7H_{12}O_5 + 3H_2O = C_8H_{18}O_7 + C_6H_{12}O_6$. With sulphuric acid, with sulphuric acid and bromine, with ferric chloride, and with potassium iodide, it gives very nearly the same reactions as the commercial brands of digitalin, although it does not give the blue reaction with Lafont's reagent. It is distinguished by the characteristic cherry red to reddish-brown coloration produced on the addition of nitric acid and a trace of cupric chloride. Its physiological action is very similar to that of the digitalis glucosides. E. W. W.

Rutin. By Fritz Wischo (*Chem. Centr.*, 1896, ii, 591; from *Pharm. Post.*, **29**, 333).—Rutin, which is obtained from rue, and quercitrin are isomeric compounds of a composition represented by Herzig's formula for the latter, $C_{36}H_{38}O_{20} + 3H_2O$. The product obtained by the decomposition of rutin with dilute mineral acids is named *isoquercetin*, and differs in physical properties from quercetin, which is similarly prepared from quercitrin. Isoquercetin is less soluble than quercetin, gives a dirty green coloration with ferric chloride which on warming turns bright red, whilst quercetin with ferric chloride forms a dark green solution which on warming becomes dark red. E. W. W.

Folia Bucco. By M. Bialobrzeski (*Chem. Centr.*, 1896, ii, 551—552; from *Pharm. Zeits. Russ.*, **35**, 353—358, 385—389, 401—405, 417—421, 433—436, 449—451).—The light petroleum extracts of *Folia Bucco longa* from *Barosma serratifolia* and of *Folia Bucco rotunda* from *B. betulina*, contain an ethereal oil besides some chlorophyll and resin. The oil, of which 1·88 per cent. is obtained from the former and 0·84 per cent. from the latter, is prepared by fractionating the acid petroleum extract under 14 mm. pressure to 130° and then distilling with steam. The resinous substance begins to boil at above 190° and has a brownish-green colour, an aromatic odour, and a bitter taste. After extraction with petroleum, the leaves, on treatment with cold alcohol, yield 3 per cent. of a brownish-green, bitter resin, insoluble in benzene and light petroleum. From the alcoholic extract of *B. serratifolia*, diosmin is deposited on the addition of sodium carbonate. Finally, by using hot 80—85 per cent. alcohol, a green acid extract is obtained which, on adding sodium carbonate, forms a precipitate of the sodium compound of diosmin, calcium carbonate, and manganese carbonate, from which diosmin is separated by treatment with 80—85 per cent. alcohol, washing with water containing 0·5 per cent. glacial acetic acid, and crystallising from hot alcohol. *B. betulina* yields 0·02 per cent. and *B. serratifolia* 0·045 per cent. of diosmin. This compound can also be obtained by washing the leaves with alcohol to which 0·2 per cent. of glacial acetic acid has been added.

The ethereal oil, which has a camphor and peppermint-like odour, boils at 178—235°, is very soluble in ether, alcohol, and benzene, and forms a green solution with ferric chloride. In the cold, it solidifies with separation of diosphenol—a phenol aldehyde which reduces oxide of silver and constitutes about 50 per cent. of the whole oil. Diosphenol may also be obtained by shaking the oil with potassium hydroxide solution. In order to free the liquid portion of the ethereal oil from diosphenol, it is fractionated under 15 mm. pressure and the portion boiling at 120—125°, which solidifies and consists mostly of the phenol, is pressed between filter paper. All the liquid fractions are freed from diosphenol by repeatedly shaking with silver oxide until the oil obtained by distilling with steam after adding sodium carbonate gives no coloration with ferric chloride. The diosphenol is thus converted into the sodium salt of *diosphenolic acid*, $OH\cdot C_6H_{14}\cdot COOH$, and is obtained as a white, amorphous, deliquescent powder insoluble in ether on treating the aqueous solution with animal charcoal, extracting with aqueous alcohol the white residue left on evaporation, again evaporating the solution, and drying in a vacuum. It can be further purified by washing with ether. Hydrochloric acid precipitates the acid from the sodium salt as a brown oil which may be purified to an almost colourless oil by converting it into the sodium salt and purifying this as above described. On fractionation under 14 mm. pressure, the liquid ethereal oil free from diosphenol yields a small distillate boiling at 64—67°, and a larger one boiling at 96—99°. After drying with potassium carbonate, these fractions boil respectively at 174—176° and 206—209° under the ordinary pressure.

Diosphenol, $OH\cdot C_6H_{14}\cdot CHO$, on crystallisation from alcohol, forms lustrous, colourless crystals having an odour like that of camphor, melts at 82°, and boils at 232° under the ordinary pressure and at 112° under 14 mm. pressure. The *oxime* melts at 156°. The phenylhydrazine compound forms a blood-red liquid which solidifies at 0°, but was not obtained pure. On reduction with sodium in an aqueous ethereal solution, diosphenol yields the *alcohol* $C_6H_{14}(OH)\cdot CH_2\cdot OH$, which melts at 159°.

By heating with alcoholic potash, diosphenol forms an *acid* which melts at 97°, and whose composition differs from that of diosphenolic acid by containing one more molecule of water.

The fraction of the oil boiling at 206—209° is a *ketone*, $C_{10}H_{18}O$, isomeric with menthone; it has a peppermint-like odour, and decolorises potassium permanganate solution. Its sp. gr. $=0{\cdot}8994$ at 18·5°, its specific rotatory power $[\alpha]_D = -6{\cdot}12°$. The *oxime* is a faintly green liquid of sp. gr. 0·9627 at 18·5°, boils at 134—135°, and has a specific rotatory power $[\alpha]_D = +2{\cdot}19°$. The bromine derivative, $C_{10}H_{17}OBr_3$, is a brown, fuming liquid.

The fraction of the oil which boils at 174—176° corresponds with terpene in composition, has a sp. gr. $=0{\cdot}8647$ at 18·5°, a specific rotatory power $[\alpha]_D = +60{\cdot}40°$, and decolorises potassium permanganate and bromine.

Diosmin forms minute, tasteless, and odourless white or yellow needles, is soluble in hot alcohol, melts at 244°, and by the action of dilute sulphuric acid yields a carbohydrate and an uninvestigated substance which melts at 197°. E. W. W.

Pharmacology of Kola. By P. Carles (*Chem. Centr.*, 1896, ii, 552—553; from *J. Pharm.*, [vi], 4, 104—108).—The valuation of kola nuts is best carried out by extraction with chloroform containing alcohol. Ten grams of the fine powder are mixed with 1 gram of calcium hydroxide and 20 grams of 80 per cent. alcohol, and dried until the weight is about 13·5 to 14 grams. The mass is then boiled for an hour with a mixture of 100 grams of chloroform and 20 grams of 90 per cent. alcohol, and this operation repeated three times. The alcohol keeps the powder in a fixed condition of hydration, dissolves the kolanine, ensures its decomposition by the lime, and prevents spirting of the liquid during evaporation. There are many substances found in plants which are analogous to Heckel's kola-red or Knebel's kolanine, which the author regards as a compound of kola-tannic acid with the kola alkaloids. If fresh, ripe, undamaged kola nuts are immersed in alcohol, they do not perceptibly colour it, hence, according to the author, the nuts contain little kolanine, which is only formed under the influence of air, light, warmth, and moisture. This oxidation, which is dependent on the action of the enzyme laccase, takes place extremely quickly, for a freshly cut surface of a broken nut becomes green instantly when moistened with tincture of guaiacum. Kolanine is very similar to cachou, and is always mixed with resin and other substances. Dried Congo nuts contain kolanine in a quantity equivalent to 20 per cent. of caffeine, the Indian nuts 16 per cent., and Dahomey nuts 20 per cent. The best solvent for kolanine is 70 per cent. alcohol. It is insoluble in chloroform, slightly soluble in water, but very easily soluble in dilute alkalis with decomposition. Lime and the alkaline earths decompose it, without dissolving it, in presence of water or boiling alcohol, hence the use of an alkali in the evaluation of the nuts. Aqueous acids decompose kolanine with production of very pure caffeine, but the author was unable to detect glucose, which Knebel and Heckel state also to be a product of the decomposition. Caffeine and theobromine constitute about one-fifth of the weight of kolanine.

The amount of kolanine in the nut or the extract is determined by extracting with cold water, then with 70 per cent. alcohol, washing the product with cold water, and drying at 100°. To estimate the alkaloids, a mixture of 1 gram with 1 gram of lime, 3 grams of chalk, and 6 grams of 70 per cent. alcohol is extracted with alcohol and chloroform. E. W. W.

Compounds from Lichens. By WILHELM ZOPF (*Annalen*, 1897, **295**, 257—300. Compare this vol., i, 362).—*Lecanora atra* (Acharius), obtained in Sicily, has been shown by Paternò to contain usnic and atralinic acids, whilst specimens collected in Italy yield usnic and atranoric acids. The author finds that the lichen derived from more northerly sources contains atranoric acid along with *lecanorol*, $C_{27}H_{30}O_9,H_2O$, identical with the substance obtained by Paternò and Crosa from *Lecanora sulphurea* (Abstr. 1894, i, 541); these two compounds are also present in *Lecanora grumosa* (Persoon). *Lecanora cenisea* (Ach.), however, contains atranoric and roccellic acids, the latter, which has the formula $C_{17}H_{32}O_4$, being the acid isolated by Schunck and by Hesse from *Roccella tinctoria*. *Lecanora sordida* (Pers.), collected in the neighbourhood of Halle, contains atranoric and zeoric acids, and it is therefore probable that the variety from an Italian source, examined by Paternò and found to contain zeorin, sordidin, and usnic acid, was not the same species. *Lecanora campestris* (Schaerer) contains atranoric acid, and *Lecanoria badia* (Pers.), stereocaulic acid; from *Lecanora varia* (Ehrh.) has been isolated psoromic acid, but no trace of atranoric acid.

Acolium tigillare (Ach.), which is identical with *Calicium tigillare* (Pers.) and with *Cyphelium tigillare* (Fries), contains rhizocarpic acid, and it is probable that this substance is also present in *A. viridulum*.

Parmelia saxatilis (L.), *var. sulcata* yields atranoric and stereocaulic acids, whilst *Parmelia tiliacea* (Hoffmann) contains atranoric and *parmelialic acid*, which crystallises in small needles, and melts, evolving gas, at 165°; the alcoholic solution of this substance develops a violet or purple-red coloration with ferric chloride, and bleaching powder gives rise to a beautiful red colour, thus affording a distinction from evernic acid, which in some respects it resembles. Parmelialic acid dissolves in alkali carbonates, liberating carbonic anhydride, and yields orcin when treated with hot, dilute caustic potash; it dissolves freely in alcohol, sparingly in chloroform, and scarcely at all in light petroleum. *Parmelia perlata* (Ach.) contains atranoric and hæmatommic acids, and not parmelin and vulpic acid, as stated by Hesse (Abstr., 1895, i, 299).

Parmelialic acid has been also obtained from *Urceolaria cretacea* (Massalongo), along with zeorin and atranoric acid; the latter substance occurs in *Parmelia aleurites* (Ach.), *Lecanora effusa* (Pers.), and *L. subfusca* (L.), being associated in the first named with stereocaulic acid, and in *L. effusa* with usnic acid. Atranoric acid is found in *Evernia furfuracea* (L.), which does not contain a trace of usnic acid as stated by Rochleder and Heldt.

Parmelia physodes (L.) is described by Gerding as yielding physodin, which melts at 125°, whilst Hesse has obtained from this lichen ceratophyllin, melting at 147°; the author is unable to confirm these statements, having obtained only atranoric acid along with two compounds, one of which melts at 188—190°, whilst the other becomes reddish-brown above 200°, and chars completely at 260°. *Dimelaena oreina* (Ach.) contains zeorin and usnic acid.

Leprarin occurs to the extent of 5 per cent. in *Lepraria latebrarum* (Ach.), and crystallises from absolute alcohol in microscopic, lustrous leaflets melting at 155°; it is insoluble in water, and but sparingly soluble in alcohol, ether, chloroform, and benzene. The alcoholic solution develops a purple red coloration with ferric chloride, but the substance is indifferent towards bleaching powder; it dissolves in concentrated sulphuric acid without undergoing change. Roccellic acid is associated with leprarin in *L. latebrarum*.

A useful summary of the author's results brings the paper to a conclusion. M. O. F.

A Reply [Tetrahydropyridine Derivatives, &c.]. By Albert Ladenburg (*Annalen*, 1897, **295**, 370—374. Compare Lipp, this vol., i, 229).—A polemical paper, in which Lipp's conclusions (*loc. cit.*) regarding the accuracy of the author's results are emphatically challenged. It is claimed that 1-methylpipecolylalkine does exhibit isomerism, which may be explained on the hypothesis of asymmetric nitrogen. M. O. F.

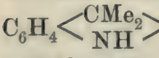
Synthesis of Piperidine, and its β-Alkylated Homologues. By J. Darnell Granger (*Ber.*, 1897, **30**, 1054—1059).—In Gabriel's process for the synthesis of piperidine, the greatest loss occurs when the γ-phenoxyvaleric acid is converted into the nitrile by means of lead thiocyanate; to avoid this, the author starts with ethylic cyanoacetate which on condensation with ethylic sodiomalonate yields *ethylic α-cyano-δ-phenoxyvalerate*, $OPh\cdot CH_2\cdot CH_2\cdot CH_2\cdot CH(CN)\cdot COOEt$, a brown oil decomposing when distilled under diminished pressure. The *acid*, which melts at 62—67°, is extremely soluble, and cannot be recrystallised; at 200°, it loses carbonic anhydride, and yields an oil identical with Gabriel's δ-phenoxyvaleronitrile and giving ε-phenoxyamylamine on reduction.

No advantage is gained by using chloromethoxypropane instead of phenylic chloropropylic ether in this reaction, the *ethylic α-cyano-δ-methoxyvalerate* formed on condensing this substance with ethylic sodiomalonate being also decomposed during distillation. *Ethylic γ-methoxypropylmalonate* is a colourless oil boiling at 254—258°. J. F. T.

Resolution of Synthetic β-Propylpiperidine into its Active Constituents. By J. Darnell Granger (*Ber.*, 1897, **30**, 1060—1065. Compare preceding abstract).—*β-Propylpiperidine*, prepared by treating β-propylchloramylamine with potash, is a clear, colourless liquid, which boils at 174° (758 mm.), and has a sp. gr. = 0·8475 at 26°. The *hydrochloride* crystallises in long, colourless needles or prisms melting at 127—129°, and the *aurochloride* in lemon-yellow needles, melting at 95—98° after recrystallisation from water. With phenylthiocarbimide it yields *phenyl-β-propylpiperidinethiocarbamide*, $C_8H_{16}N\cdot CS\cdot NHPh$, which forms stellate groups of needles melting at 90·5°.

The resolution of β-propylpiperidine into its active constituents is effected by Marckwald's method, that is through the tartrates, *l-β-propylpiperidine d-tartrate* is obtained in large white prisms melting at 161°, when a solution of *d*-tartaric acid is added to β-propylpiperidine, and crystallisation started by the addition of a crystal of coniine tartrate. The base *l-β-propylpiperidine*, obtained from this tartrate by treatment with potash, boils at 174° (752·5 mm.), and has a rotation $a_D = -5° 44'$, the *hydrochloride* melts at 147°.

d-β-Propylpiperidine l-tartrate, prepared in the same way, crystallises in long prisms melting sharply at 158°, and yielding, on treatment with potash, *d-β-propylpiperidine*, a substance showing the rotation $a_D = 5° 55'$; its *hydrochloride* melts at 147°. J. F. T.

Indolinones. II. By KARL BRUNNER (*Monatsh.*, 1897, 18, 95—122. Compare this vol., i, 100).—3′ : 3′-*Dimethyl-2′-indolinone*,  $C_6H_4<{CMe_2 \atop NH}>CO$, was prepared by heating isobutyrylphenylhydrazide with three times its weight of quicklime for 2 hours at 170—200°, boiling the product for an hour with excess of hydrochloric acid in a reflux apparatus, and filtering off the indolinone. It crystallises in rhombic prisms of two different habits [$a : b : c = 0·8496 : 1 : 0·7219$], which were examined exhaustively from the crystallographical point of view; it melts at 151°, and boils at 302·5° under 759 mm. pressure. It forms no crystalline salts with acids but it gives a *silver* derivative,

$$C_{10}H_{10}AgNO,$$

which, when heated at 60° with methylic iodide in ethereal solution, yields a *lactime-ether*, $C_6H_4<{CMe_2 \atop N}\geqslant C\cdot OMe$, melting at 62°; and when heated with methylic iodide and sodium methoxide for 16 hours at 100—120°, it yields a lactam-ether, $C_6H_4<{CMe_2 \atop NMe}>CO$, (1′ : 3′ : 3′-trimethyl-2-indolinone), which has already been prepared. When boiled with acetic anhydride, it yields an *acetyl* derivative,

$$C_{10}H_{10}AcNO,$$

melting at 105°; with sodium nitrite, in cooled acetic acid solution, it yields a yellowish *nitroso*-derivative, $NO\cdot C_{10}H_{10}NO$, melting and decomposing at 60°; with nitric acid in acetic acid solution, it yields a yellowish-red *nitro*-derivative, $NO_2\cdot C_{10}H_{10}NO$, melting at 258° (together with a small quantity of another nitro-product which is yellow and melts at 186°); and in acetic acid solution it yields, with bromine water, a *dibromo*-derivative, $C_{10}H_9Br_2NO$, identical with the compound obtained from the trimolecular base $(C_{10}H_{11}N)_3$ (Abstr., 1896, i, 169).

3′ : 3′-Dimethyl-2′-indolinone can be reduced with sodium in boiling amyl-alcoholic solution to 3′ : 3′-*dimethylindoline*, $C_6H_4<{CMe_2 \atop NH}>CH_2$, which is more conveniently prepared by reducing in the same manner the above-mentioned trimolecular base. This indoline melts at 34—35°, and boils at 226—228° under 743 mm. pressure; it is best isolated by means of the sparingly soluble compound which it yields with potassium ferrocyanide. The *hydrochloride* turns yellow at 100° and melts at 172°; the reddish *platinochloride* melts and decomposes at about 200°; the *oxalate*, $C_{10}NH_{13},C_2H_2O_4$, melts at 139°. With nitrous acid, it yields a yellowish *nitroso*-derivative, $NO{\cdot}C_{10}NH_{12}$, which melts at 66°, and also, in the presence of excess of nitrous acid, a second compound, also yellowish, that melts at 192°, and is probably a *nitro-nitroso*-derivative, for it is formed by the action of strong nitric acid on the nitroso-compound. The indoline is oxidised by many oxidising agents; bromine water converts it into the dibromo-3′ : 3′-dimethyl-2′-indolinone mentioned above. It represents the third possible dimethylindoline, the other two being already known (2′ : 2′, Paal and Laudenheimer, Abstr., 1893, i, 38; 2′ : 3′, Steche, Abstr., 1887, 588; 1888, 298); that of Ciamician and Piccinini (this vol., i, 102) may be identical with any one of these three. C. F. B.

Quinolinesulphonic Acids. By ADOLPH CLAUS (*J. pr. Chem.*, 1897, [ii], **55**, 225—237).—Quinoline-4-sulphonic acid differs from the 1-isomeride in that it can be brominated without at the same time losing the sulphonic group. This is effected by dissolving it in strong hydrobromic acid, and adding a solution of bromine in acetic acid; the product is identical with the 3′-bromoquinoline-4-sulphonic acid of Claus and Schmeisser (Abstr., 1890, 266; apparently described there as 4′ : 4-bromoquinolinesulphonic acid). If the acid is brominated in the absence of water, the bromine being used either alone or in chloroform solution, the sulphonic group is lost, and a mixture of derivatives is obtained, as in the case of the 1-isomeride; the 4-sulphonic acid appears to yield 1 : 4 : 3′, the 1-isomeride 1 : 3 : 3′-tribromoquinoline, melting at 168·5° and 169—170° respectively, whilst both yield 1 : 3 : 4 : 3′-tetrabromoquinoline, melting at 205°. It is difficult to isolate and identify these products, for when obtained with constant melting point, they are found to be still impure.

Tetrahydroquinoline-4-sulphonic acid, $C_9NH_{10}{\cdot}SO_3H + H_2O$ (Lellmann, Abstr., 1888, 297), yields *ammonium*, with H_2O; *potassium*, with $\frac{1}{2}H_2O$; *barium*, with $3\frac{1}{2}H_2O$; *calcium*, with $2\frac{1}{2}H_2O$; *copper*, with $3H_2O$; *nickel*, with $3\frac{1}{2}H_2O$; *lead*, with $2\frac{1}{2}H_2O$; and anhydrous *silver* salts. When brominated, either with bromine alone, or in acetic acid or chloroform solution, the acid yields amongst other products 2-*bromo-tetrahydroquinoline*-4-*sulphonic acid*; this melts at 285°, and when brominated in aqueous solution with excess of bromine, appears to yield 3 : 4 : 3′-*tribromoquinoline* melting at 148°, together with other products. C. F. B.

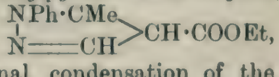
Carbazole Derivatives. By EMIL VOTOČEK (*Chem. Centr.*, 1896, ii, 490; from *Rozpravy české akad.*, 1896, **5**, Kl. ii, Nr. 22).—Carbazole, when nitrated in glacial acetic acid at 80° with nitric acid of sp. gr. 1·38 (1 Mol.), yields *mononitrocarbazole*, which forms yellow flakes or needles melting at 210°. When Witt's method of nitration is employed, dinitro-derivatives are not obtained, as in the case of diphenylamine, but two mononitrocarbazoles are formed, the one, brown crystals melting at 210°, the other, lemon-yellow needles melting at 184°. By the action of a mixture of nitric acid (sp. gr. 1·4) with alcohol and glacial acetic acid on nitrosocarbazole, a dinitro-derivative is obtained which does not melt below 306°. The *diamidocarbazole* prepared from this crystallises in grey, silvery scales, decomposes above 260°, is slightly soluble in benzene, toluene, xylene, and alcohol, and its salts show a strong lignin reaction.

On treatment with excess of bromine, carbazole forms *tetrabromocarbazole*, which melts at 220°, and on boiling with nitric acid of sp. gr. 1·4 is converted into *tetrabromodinitrocarbazole*, which melts at 294°. By heating with carbon tetrachloride at 220°, a blue dye of the triphenylmethane type is formed by condensation. The condensation products with formaldehyde and benzaldehyde were not obtained in a crystalline form. In presence of concentrated sulphuric acid, carbazole gives, with benzaldehyde, a carmine red solution, which on pouring into water turns blue, with paranitrobenzaldehyde a ruby to magenta red coloration, with metanitrobenzaldehyde a dark red solution which turns green on addition of water, with vanillin a crimson red solution turning violet on dilution, with furfuraldehyde a carmine red to violet, and with glucose a violet coloration. A drop of concentrated sulphuric acid added to a hot solution of carbazole in acetic acid produces a violet coloration, and with a solution of carbazole and glucose a strong blue coloration. E. W. W.

The Pyrazole Series. By Ludwig Claisen (*Annalen*, 1897, **295**, 301—324. Compare Abstr., 1894, i, 345).—The author has already shown that phenylhydrazine undergoes condensation with ethylic ethoxymethylenemalonate, yielding a phenylhydrazide, which is converted at 170° into ethylic 1 : 5 : 4-phenylpyrazolonecarboxylate (Abstr., 1895, i, 193); the present investigation deals with the action of phenylhydrazine on ethylic ethoxymethyleneacetate, and ethoxymethyleneacetylacetone.

[With C. Niegemann and F. Thomas.]—When phenylhydrazine and ethylic ethoxymethyleneacetate are mixed in ethereal solution at − 10°, the *phenylhydrazide*, $C_6H_8O_3{:}CH{\cdot}NH{\cdot}NHPh$, or $C_6H_9O_3{\cdot}CH{:}N{\cdot}NHPh$, separates in aggregates of small, colourless needles, and melts at 87—88°; it loses the elements of water under the influence of glacial acetic acid and concentrated hydrochloric acid, the same effect being produced when the substance is heated on the water bath.

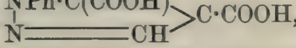
Ethylic 1 : 5-*phenylmethylpyrazole*-4-*carboxylate*,

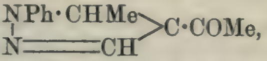
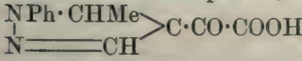
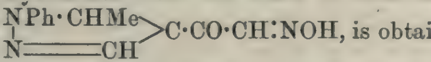


$$\left.\begin{array}{l}\mathrm{NPh{\cdot}CMe}\\ \mathrm{N{=\!=\!=}CH}\end{array}\right>\mathrm{CH{\cdot}COOEt},$$

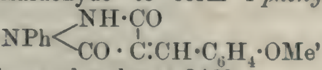
the product of internal condensation of the foregoing compound, crystallises from light petroleum in large, transparent, tabular prisms, melting at 55—56°; the *acid* crystallises from boiling water in short prisms, and melts at 167—168°. The *silver* salt resists the action of light, and the *calcium* salt, crystallising in leaflets, contains $2H_2O$, which is removed at 150°; the *methylic* salt separates from methylic alcohol in colourless prisms, and melts at 71°. 1 : 5-*Phenylmethylpyrazole*, $C_{10}H_{10}N_2$, produced on distilling the carboxylic acid, boils at 260—261° under a pressure of 753 mm., and has a sp. gr.

= 1·085 at 15°; it is therefore identical with the base obtained by distilling 1:5-phenylmethylpyrazole-3-carboxylic acid (Abstr., 1894, i, 346).

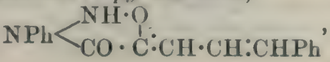
1-*Phenylpyrazole*-4:5-*dicarboxylic acid*,  $\left.\begin{array}{l}\mathrm{NPh{\cdot}C(COOH)}\\ \mathrm{N{=\!=\!=}CH}\end{array}\right>\mathrm{C{\cdot}COOH}$, is prepared by oxidising a boiling alkaline solution of phenylmethylpyrazolecarboxylic acid with potassium permanganate, and, after repeated crystallisation from hot water, melts at 215—216°; neither the acid nor its salts can be regarded as identical with the so-called 4:5-dicarboxylic acid of Balbiano and Severinini. The acid crystallises in short prisms, and yields a fluorescent compound with resorcinol and sulphuric acid; the *hydrogen barium* salt crystallises in small needles, and the *silver* salt is amorphous. The *methylic* salt crystallises from methylic alcohol in silky needles, melting at 75—76°, and is converted by ammonia into the *monamide* and *diamide* which crystallise in needles, and melt at 186° and 253—255°, respectively; the *dianilide* dissolves with difficulty in alcohol and ethylic acetate, and melts at 205—206°. Rapid distillation of the dicarboxylic acid converts it into 1:4-phenylpyrazolecarboxylic acid, which melts at 221—222°, 1-phenylpyrazole being produced when the dicarboxylic acid is boiled in a reflux apparatus.

4:1:5-*Acetylphenylmethylpyrazole*,  $\left.\begin{array}{l}\mathrm{NPh{\cdot}CHMe}\\ \mathrm{N{=\!=\!=}CH}\end{array}\right>\mathrm{C{\cdot}COMe}$, obtained by the action of phenylhydrazine on ethoxymethyleneacetylacetone in ethereal solution, crystallises from light petroleum in colourless prisms; it melts at 107—108°, and boils at 331—333° (corr.), under a pressure of 745 mm. The *methiodide* crystallises in small, colourless prisms, and melts at 166°. The *ketonic acid*,  $\left.\begin{array}{l}\mathrm{NPh{\cdot}CHMe}\\ \mathrm{N{=\!=\!=}CH}\end{array}\right>\mathrm{C{\cdot}CO{\cdot}COOH}$, produced on oxidising the substance with potassium permanganate, crystallises from water in white needles melting at 166°; the *phenylhydrazone* melts at 207—208°, and the *silver* salt crystallises from hot water in lustrous needles. The *isonitrosoketone*,  $\left.\begin{array}{l}\mathrm{NPh{\cdot}CHMe}\\ \mathrm{N{=\!=\!=}CH}\end{array}\right>\mathrm{C{\cdot}CO{\cdot}CH{:}NOH}$, is obtained on treating the ethereal solution of the pyrazole derivative with sodium and amylic nitrite; it crystallises from ethylic acetate in colourless, silky needles, and melts at 192°. Caustic soda resolves the isonitrosoderivative into hydrogen cyanide and 1:5:4-phenylmethylpyrazolecarboxylic acid.

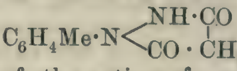
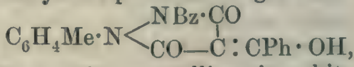
M. O. F.

Derivatives of 1-Phenyl-3:5-pyrazolidone and 1-Paratolyl-3:5-pyrazolidone. By TH. ASHER (*Ber.*, 1897, **30**, 1018—1024).—1-Phenyl-3:5-pyrazolidone (Michaelis and Burmeister, *Ber.*, **25**, 1502) readily condenses with anisaldehyde to form 1-*phenyl*-4-*methoxybenzylidene*-3:5-*pyrazolidone*,  $\mathrm{NPh}<\begin{array}{l}\mathrm{NH{\cdot}CO}\\ \mathrm{CO{\cdot}C{:}CH{\cdot}C_6H_4{\cdot}OMe}\end{array}$, which crystallises in yellowish-red needles, and melts at 246°.

1-*Phenyl*-4-*cinnamylidene*-3:5-*pyrazolidone*,

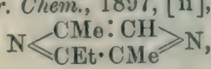
 $\mathrm{NPh}<\begin{array}{l}\mathrm{NH{\cdot}O}\\ \mathrm{CO{\cdot}C{:}CH{\cdot}CH{:}CHPh}\end{array}$,

is obtained in a similar manner from cinnamaldehyde and melts at 252°, whilst 4-*dibromophenylpyrazolidone*, obtained by the direct action of bromine, crystallises in golden yellow needles melting at 243°. When phenylpyrazolidone is boiled with chloroform, a *condensation product* of unknown constitution is formed which melts at 303°.

1-*Paratolyl*-3 : 5-*pyrazolidone*,  $C_6H_4Me\cdot N\langle{}^{NH\cdot CO}_{CO\cdot CH_2}$, prepared by the hydrolysis of the product of the action of paratolylhydrazine on ethylic chloromalonate, crystallises in white plates melting at 204°; the *basic lead* salt, $C_{10}H_9N_2O_2\cdot Pb\cdot OH$, is a yellow precipitate. 1-*Paratolyl*-4-*benzylidene*-3 : 5-*pyrazolidone* melts at 253°; the corresponding acetone derivative, *paratolyl*-4-*isopropylidenepyrazolidone*, melts at 174°. *Tolyl*-4-*isonitrosopyrazolidone* crystallises in red needles melting at 182°, and is soluble in alkalis. 1-*Paratolyl*-3 : 5-*pyrazolidone*-4-*phenylhydrazone* is obtained by the action of diazobenzene chloride on the pyrazolidone, and crystallises in golden yellow plates melting at 234°. 2 : 4-*Dibenzoyl*-1-*paratolylpyrazolidone*,  $C_6H_4Me\cdot N\langle{}^{NBz\cdot CO}_{CO-C:CPh\cdot OH}$, the constitution of which is not quite certain, crystallises in white plates melting at 133°. 1-*Paratolyl*-4-*dibromopyrazolidone* crystallises in prisms melting at 174°. Tolylpyrazolidone also appears to combine with a molecule of tolylhydrazine to form an additive *compound*, $C_{17}H_{20}N_4O_2$, which crystallises in white plates melting at 182°, and has basic properties.

Malonyl chloride reacts with phenylhydrazine to form malonyl dihydrazide, $CH_2(CONH\cdot NHPh)_2$, melting at 184°, and with paratolylhydrazine hydrochloride to form tolylpyrazolone in small quantity.

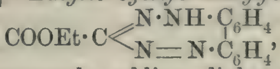
A. H.

Pyrazinetricarboxylic Acids and their Products of Decomposition. By CARL STOEHR and W. DETERT (*J. pr. Chem.*, 1897, [ii], 55, 248—262).—2 : 5-Dimethyl-3-ethylpyrazine,  $N\langle{}^{CMe:CH}_{CEt\cdot CMe}\rangle N$, (compare Abstr., 1893, i, 486), when oxidised with permanganate on the water bath, is to a large extent completely oxidised, but yields some *pyrazine*-2 : 3 : 5-*tricarboxylic acid*, $C_4N_2H(COOH)_3 + 2H_2O$. This melts at 164°, but when anhydrous, it melts and decomposes at 180°. The *silver*, $C_7HN_2O_6Ag_3 + H_2O$; *barium*, with $4H_2O$; *calcium*, with $12H_2O$; *strontium*, with $12H_2O$; and *cadmium*, with $9H_2O$ salts were prepared; with the exception of the silver salt, these retain some of their water of crystallisation at 160°.

The acid itself loses carbonic anhydride when boiled with water; after boiling for 2—3 days, the products are 2 : 5-pyrazinedicarboxylic acid (*loc. cit.*; also Wolff, *ibid.*, p. 373) and an isomeric acid. Of the first, the *potassium*, $C_4N_2H_2(COOK)_2$; *sodium*, and *strontium*, with $5H_2O$, salts were prepared. The second product, $C_4N_2H_2(COOH)_2 + 2H_2O$, is probably *pyrazine*-3 : 5-*dicarboxylic acid*, for it does not yield an anhydride when heated with acetic anhydride, as we should expect a 2 : 3-dicarboxylic acid—the only other isomeride possible—to do. The acid which melts and decomposes at 217—218°, crystallises in monoclinic prisms; $a : b : c = 1\cdot0529 : 1 : ?$; $\beta = 62°\ 43\frac{1}{2}'$. It is more soluble in alcohol than the 2 : 5-acid, and its salts are rather more soluble; several of these were prepared, and the *silver* salt, $C_6H_2N_2O_4Ag_2 + H_2O$, which retains its water obstinately, was analysed. C. F. B.

Action of Diphenyltetrazochloride on Ethylic Acetoacetate. By Edgar Wedekind (*Annalen*, 1897, **295**, 324—339).—It has been shown that diazobenzene chloride converts the sodium derivative of ethylic acetoacetate into ethylic benzeneazoacetoacetate, whilst the presence of 2 molecular proportions of the azo-compound along with excess of alkali, gives rise to ethylic formazylformate (Abstr., 1893, i, 84); the author has therefore studied the action of diazotised benzidine on the salt.

[With Paul Nissen.]—*Ethylic cycloformazylformate*,

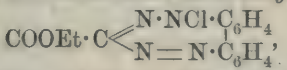


$$\mathrm{COOEt\cdot C}\left<\begin{array}{l}\mathrm{N\cdot NH\cdot C_6H_4}\\ \mathrm{N{=}N\cdot C_6H_4}\end{array}\right.,$$

is obtained by simultaneously adding diphenyltetrazochloride and ethylic acetoacetate (1 mol.) to aqueous caustic potash at 0°, and is purified by precipitation with light petroleum from a solution in chloroform; it is an amorphous, reddish-brown powder, which becomes dark at 180°, sinters at 200°, and melts at 280°. The solution in concentrated hydrochloric and sulphuric acids is intensely green.

The *ethylic* salt of dibutanonic acid diphenyldihydrazone (*ethylic diacetylglyoxylate diphenyldihydrazone*), $C_{12}H_8[NH\cdot N\colon C(COMe)\cdot COOEt]_2$, is produced when diphenyltetrazochloride acts on two molecular proportions of ethylic acetoacetate, and crystallises from alcohol in small, yellow needles melting at 197—198°; towards alkalis, its behaviour resembles that of ethylic benzeneazoacetoacetate, dissolving in the gently heated agent, precipitation occurring as the temperature rises. The solution in concentrated sulphuric acid is yellowish-brown, and becomes deep red when treated with ferric chloride; with diazobenzene chloride (2 mols.), the alkaline solution yields a reddish-brown *compound* which melts at 235—240°.

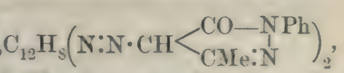
Ethylic cyclodiphenyltetrazoliumchloridecarboxylate,



$$\mathrm{COOEt\cdot C}\left<\begin{array}{l}\mathrm{N\cdot NCl\cdot C_6H_4}\\ \mathrm{N{=}N\cdot C_6H_4}\end{array}\right.,$$

is obtained by oxidising ethylic cycloformazylformate with amylic nitrite and alcoholic hydrogen chloride, and sinters indefinitely at 206°; the alcoholic solution gives a yellow precipitate with picric acid or gold chloride, and concentrated sulphuric acid slowly produces a brownish-red solution. Reducing agents regenerate ethylic cycloformazylformate.

Bisphenylmethylpyrazoloneazodiphenyl,



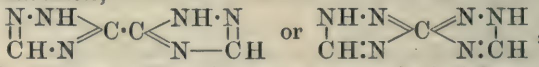
$$\mathrm{C_{12}H_8}\left(\mathrm{N\colon N\cdot CH}\left<\begin{array}{l}\mathrm{CO{-}NPh}\\ \mathrm{CMe\colon N}\end{array}\right.\right)_2,$$

obtained by heating the ethylic salt of dibutanonic acid diphenyldihydrazone with phenylhydrazine dissolved in glacial acetic acid, is a bright red, micro-crystalline powder, which melts and evolves gas at 289°; it dissolves with extraordinary difficulty in common solvents, and forms a deep red solution in concentrated hydrochloric acid. 1 : 3-Phenylmethylpyrazolone-4-azobenzene melts at 155°.

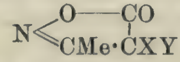
Diphenyltetrazochloride combines with malonic acid, yielding a reddish-brown *compound* which is insoluble in all media excepting concentrated sulphuric acid. M. O. F.

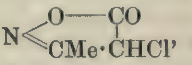
Derivatives of Ditriazole from Cyanophenylhydrazine and Cyanohydrazine. By ERICH L. RINMAN (*Ber.*, 1897, **30**, 1193—1195).—Dicyanophenylhydrazine has the constitution $NHPh\cdot N\colon C(CN)\cdot NH_2$, and when mixed with phenylhydrazine (1 mol.) and a very small quantity of alcohol, it yields cyanophenylhydrazine; the author therefore ascribes to the latter substance the formula $C_2(NH_2)_2(N\cdot NHPh)_2$.

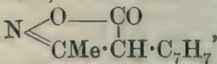
When cyanohydrazine is treated with boiling formic acid in a reflux apparatus, *ditriazole*,



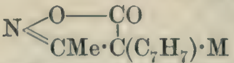
is produced; this crystallises from a mixture of glacial acetic acid and concentrated hydrochloric acid in colourless scales, and sublimes above 300° in prismatic crystals. M. O. F.

Derivatives of Isoxazolone. By ROBERT SCHIFF and G. VICIANI (*Ber.*, 1897, **30**, 1159—1166).—By eliminating alcohol from the oxime of derivatives o ethylic acetoacetate, a large number of compounds of the type  can be prepared.

Methylchlorisoxazolone,  prepared from the oxime anilide of ethylic α-chloracetoacetate, melting at 112°, by treating it with sodium hydroxide solution; it separates from hot benzene in colourless crystals melting at 86—87°.

The oximeanilide of ethylic benzylacetoacetate, at the moment of its formation, passes into *methylbenzylisoxazolone*, , which crystallises from dilute methylic alcohol in glistening prisms melting at 106°, and is acidic, forming two kinds of salts of the types

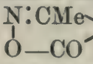
$$OH\cdot N\colon CMe\cdot CH(C_7H_7)\cdot COOM$$

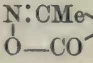
and  respectively, the salts of the alkali metals having the former, whilst those of the heavy metals have the latter constitution; the *phenylhydrazone* of *methylisoxazolone* melts and decomposes at 192°, the *orthanisylhydrazone* melts at 172—173°, the *orthotolylhydrazone* at 154—155°, the *paratolylhydrazone* at 202°, the *α-naphthylhydrazone* at 168—170°, the *β-naphthylhydrazone* at 200°, and the *paroxyphenylhydrazone* at 219—220°, with decomposition.

J. F. T.

Isoxazolones. By RUDOLF UHLENHUTH (*Annalen*, 1897, **296**, 33—62).—Phenylisoxazolone is prepared by Hantzsch's method (Abstr., 1891, 740), and, according to the author, melts at 152°; the *potassium* derivative crystallises in colourless, nacreous scales, the *barium* and *calcium* derivatives are anhydrous, whilst the *strontium* derivative contains $1H_2O$. The *silver* derivative is sensitive towards light, and the *cadmium* derivative contains $5H_2O$; the *copper, zinc* and *lead* derivatives have been also prepared. The *methylamine* and *ethylamine* derivatives are crystalline, and melt at 95° and 108° respectively, the *dimethylamine* and *diethylamine* derivatives are oils, and decompose in the desiccator, whilst the *aniline* derivative crystallises in colourless, quadratic leaflets, and melts at 110—111°; the *toluidine* and *phenylhydrazine* derivatives melt and decompose at 117° and 153° respectively, and the piperidine derivative is an oil. The silver derivative of phenylisoxazolone acts on alkylic iodides, forming the *methyl* and *ethyl* derivatives, which melt at 78° and 76° respectively.

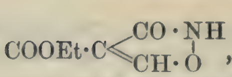
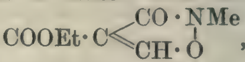
The preparation of methylisoxazolone is attended with some difficulties, but small quantities may be obtained by heating the oxime of ethylic acetoacetate with ammonia, and decomposing with hydrochloric acid the derivative of methylisoxazolone so produced; this substance, the properties of which have been described by Hantzsch, melts at 169—170°, and is bimolecular in naphthalene. The *potassium* derivative crystallises in colourless, monoclinic plates, and the *methylamine*, *ethylamine*, *dimethylamine*, and *diethylamine* derivatives are also crystalline, and melt at 177—178°, 135—136°, 109—111°, and 112—114° respectively; the *aniline*, *naphthylamine*, and *phenylhydrazine* derivatives melt at 150—151°, 116°, and 102—103° respectively. The *methyl* derivative crystallises in transparent, four-sided prisms, and melts at 74—75°; the *ethyl* derivative melts at 90—91°.

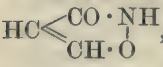
Dimethylisoxazolone,  $\left.\begin{array}{l}\mathrm{N{:}CMe}\\ \;|\\ \mathrm{O{-}CO}\end{array}\right>\mathrm{CHMe}$, is obtained by agitating a concentrated solution of hydroxylamine hydrochloride to which the calculated amount of caustic soda has been added with ethylic methylacetoacetate, the liquid being cooled meanwhile by a freezing mixture; the ethereal salt is dissolved during the process, and concentrated hydrochloric acid is then added in sufficient quantity to liberate dimethylisoxazolone as a crystalline precipitate. It melts and decomposes at 123—124°, and dissolves readily in alkalis and alkali carbonates; ferric chloride develops a reddish-brown coloration with the alcoholic solution. The *ammonium* derivative crystallises in aggregates of concentric prisms, and loses ammonia in moist air; the *hydrogen barium* derivative crystallises in needles containing $5\frac{1}{2}H_2O$, and melts at 167—175°. The *silver* derivative melts and decomposes at 218°, and the *hydrogen silver* derivative resists the action of light, and melts at 197°.

Methylethylisoxazolone,  $\left.\begin{array}{l}\mathrm{N{:}CMe}\\ \;|\\ \mathrm{O{-}CO}\end{array}\right>\mathrm{CHEt}$, is prepared from hydroxylamine and ethylic ethylacetoacetate in the same way as the foregoing substance; it crystallises in white needles or prisms, melts at 50°, and develops a reddish-brown coloration with ferric chloride. The *barium* derivative contains $5\frac{1}{2}H_2O$, which is lost at 110°, and the *hydrogen silver* derivative is crystalline, and melts at 154°. M. O. F.

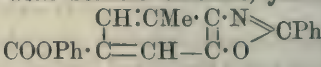
Action of Hydroxylamine on Ethylic Dicarboxyglutaconate.

By SIEGFRIED RUHEMANN (*Ber.*, 1897, **30**, 1083—1087).—When ethylic dicarboxyglutaconate is suspended in alcohol and treated with hydroxylamine hydrochloride, a reaction takes place, and *ethylic pyroxolone-*

carboxylate,  $\mathrm{COOEt{\cdot}C}{<}\begin{matrix}\mathrm{CO\cdot NH}\\ \mathrm{CH\cdot O}\end{matrix}$, is produced, which crystallises in colourless prisms, and melts and decomposes at 168°. It gives a deep red coloration with ferric chloride, and possesses well-marked acid properties. The *silver salt* crystallises in lustrous plates, and decomposes suddenly when heated. The *ammonium salt* crystallises in long needles. When boiled with aqueous potash, the ethylic salt is decomposed with formation of malonic acid, ammonia, carbonic anhydride, and alcohol. When the silver salt is heated with methylic iodide, *ethylic methylpyroxolonecarboxylate,*  $\mathrm{COOEt{\cdot}C}{<}\begin{matrix}\mathrm{CO\cdot NMe}\\ \mathrm{CH\cdot O}\end{matrix}$, is produced, which crystallises in colourless prisms, melting at 96—97°, gives no coloration with ferric chloride, does not yield metallic salts, and is decomposed by potash with formation of methylamine. This reaction proves that the original ethylic pyroxolonecarboxylate contains an imido-group.

The author proposes to give the name pyroxolone to the group  $\mathrm{HC}{<}\begin{matrix}\mathrm{CO\cdot NH}\\ \mathrm{CH\cdot O}\end{matrix}$, from which this substance is derived. A. H.

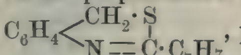
Derivatives of Amido-orcinol and of Methylamido-orcinol.

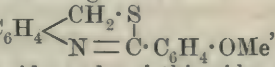
By Frs. Henrich (*Ber.*, 1897, 30, 1104—1110. Compare this vol., i, 404).—Amido-orcinol, when warmed with benzoic chloride, yields *parabenzoyloxy-β-phenylorthotoluoxazole,*  $\mathrm{COOPh{\cdot}C}\begin{matrix}\mathrm{CH{:}CMe\cdot C\cdot N}\\ \mathrm{{=}CH{-}C\cdot O}\end{matrix}{>}\mathrm{CPh}$; this crystallises from absolute alcohol in colourless, long, thin plates, melts at 133°, and is readily soluble in ether, benzene, chloroform, and ethylic acetate, also in hot alcohol or hot acetic acid. *Parahydroxy-β-phenylorthotoluoxazole,* obtained by the action of alcoholic potash on the above benzoyl derivative, crystallises in long plates, melts at 239—239·5°, and is only sparingly soluble in cold alcohol, benzene, or ether. When warmed with acetic anhydride, it yields an *acetyl* derivative melting at 113—114°, which is readily soluble in ether and benzene.

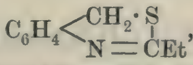
When amido-orcinol is warmed with acetic anhydride, the chief product is *triacetylamido-orcinol,* which crystallises from dilute alcohol in colourless plates. It melts at 98—99°, and is readily soluble in alcohol, benzene, acetone, and chloroform.

Diacetylmethylamido-orcinol is obtained by the action of anhydrous sodium acetate and acetic anhydride on methylamido-orcinol; it crystallises from dilute alcohol in large twinned plates, melts at 108—109°, and is extremely readily soluble in benzene, chloroform, and acetic acid. An alkaline solution of methylamido-orcinol is readily oxidised either by the air or by hydrogen peroxide to a compound, $C_{15}H_{14}O_3N_2$, which crystallises in dark red needles, and melts at 253°; the authors have proved that this compound contains only one methoxy-group. It is only sparingly soluble in alcohol, ether, or cold benzene, practically insoluble in light petroleum, but more readily soluble in warm benzene, acetic acid, or ethylic benzoate. It is soluble in concentrated sulphuric acid, yielding a deep red solution. Nitrous acid develops a deep blue colour, which slowly disappears.

This compound, and also those obtained by the oxidation of amido-orcinol, are being further investigated. J. J. S.

Derivatives of Phenopenthiazole. By HEINRICH KIPPENBERG (*Ber.*, 1897, **30**, 1141—1147).—Of the two methods for the preparation of μ-alkylphenopenthiazoles devised by Gabriel and Posner (Abstr., 1895, i, 191), that from orthamidobenzylic alcohol and the acid chloride or anhydride is the more suitable when the formation of fatty substituted compounds are desired; whilst the second method, namely, melting orthamidobenzylic chloride hydrochloride with thiamides, is best adapted for the preparation of aromatic derivatives. *μ-Paratolylphenopenthiazole*  $C_6H_4{<}\begin{matrix}CH_2\cdot S\\ N=C\cdot C_7H_7\end{matrix}$, prepared by the latter method, crystallises from dilute alcohol in microscopic needles melting at 109—110°, and *μ-orthotolylphenopenthiazole* from amidobenzylicbromide hydrobromide, and orthotolylthiamide in pale yellow scales softening at 54·5—56°.

μ-Paramethoxyphenylphenopenthiazole,  $C_6H_4{<}\begin{matrix}CH_2\cdot S\\ N=C\cdot C_6H_4\cdot OMe\end{matrix}$, from the hydrochloride of amidobenzylic chloride and anisthiamide, melts at 124·5° after recrystallisation from dilute alcohol; it gives neither a platinum nor a gold salt.

μ-Ethylphenopenthiazole,  $C_6H_4{<}\begin{matrix}CH_2\cdot S\\ N=CEt\end{matrix}$, can be prepared from thiopropionamide and orthamidobenzylicbromide hydrobromide, but is best obtained from amidobenzylic alcohol and propionic anhydride, subsequently treating the product with phosphorous pentasulphide; it boils at 270—272° (758 mm.), and yields a *hydrobromide* melting at 180—181°, a *picrate* which crystallises from alcohol in yellowish-red prisms melting at 135—136°, and also a *platinochloride.* In the formation of μ-ethylphenopenthiazole, a crystalline compound is also produced which separates from absolute alcohol in clusters of glistening needles melting at 190—191°; it is evidently *orthopropionylamidobenzylic bisulphide,* $C_{20}H_{24}O_2N_2S_2$, since it is identical with the compound produced from orthamidobenzylic bisulphide and propionic anhydride. *μ-Propylphenopenthiazole,* prepared from orthamidobenzylic alcohol and butyric anhydride in the usual way, boils at 282—284° (27 mm.) and yields a *picrate* crystallising from hot alcohol in yellow needles melting at 142—145°. J. F. T.

Action of Tannin and Gallic Acid on some Alkaloids. By WILLIAM OECHSNER DE CONINCK (*Compt. rend.*, 1897, **124**, 773—776).—An aqueous solution of tannin immediately precipitates pure and anhydrous nicotine, and an alcoholic solution precipitates nicotine from its solution in alcohol. Ethereal solutions behave in the same way. Gallic acid has no action on pure nicotine, but in presence of water a deep orange-red coloration is developed more rapidly than with tannin.

With cicutine or its aqueous solutions, neither dry tannin nor dry gallic acid produces any reaction, but with the aqueous solutions a blood-red colour soon develops. An aqueous solution of tannin precipitates pure and anhydrous cicutine, and alcoholic or ethereal solutions precipitate the corresponding solutions of the alkaloid. The reactions are somewhat sensitive, but nicotine is precipitated by tannin from much more dilute solutions than cicutine. C. H. B.

Alums of Nitrogenous Bases. By N. A. ORLOFF (*Chem. Centr.*, 1896, ii, 590—591; from *Pharm. Zeit. Russ.*, **35**, 465—468, 481—484, 497—498).—The author has confirmed the general applicability of Kirschmann's method of forming alkaloid alums. A solution containing the sulphates of the alkaloid and of aluminium or chromium was evaporated at 50° to a small volume and allowed to crystallise in a cool place. If an alum has been formed, octahedral crystals separate on adding a crystal of potash alum. Solutions which do not yield alums on further concentration deposit aluminium sulphate and eventually the sulphate of the alkaloid. Alums of *piperidine*, *coniine*, *cocaine*, *atropine*, *quinine* and *sparteine* were prepared, whilst pyridine, pilocarpine, berberine, morphine, codeine, and chelerythrine did not yield alums. Thus the alkaloids derived from hydropyridine form alums, but the pyridine derivatives are incapable of doing so. Carbamide does not form an alum, but *allylcyanamide* prepared from thiosinamine by the action of oxide of lead or of oxide of mercury, forms an easily crystallisable alum when it is dissolved in dilute sulphuric acid, mixed with aluminium sulphate, evaporated at 30—40° to a syrup, and allowed to stand twelve hours.

Asparagine alum, $(C_4H_8N_2O_3)_2,H_2SO_4,Al_2(SO_4)_3 + 24H_2O$, forms octahedral crystals. E. W. W.

Cuskhygrine Hydrate. By CARL T. LIEBERMANN and FRITZ GIESEL (*Ber.*, 1897, **30**, 1113—1115. Compare Abstr., 1895, i, 310). —*Cuskhygrine hydrate*, $C_{13}H_{24}N_2O + 3\frac{1}{2}H_2O$, is obtained from a moist ethereal solution of the base, but if the solution is dried with potassium carbonate, the oily base itself is formed. It crystallises in colourless needles, melts at 40—41°, and has the same solubilities as cuskhygrine itself. The hydrate may easily be obtained as a hard, crystalline mass by adding 21·4 per cent. of water to the base. It begins to lose its water on exposure to the air, more readily when placed over potash, or when heated. The hydrate is capable of absorbing carbonic anhydride, yielding an unstable carbonate.

J. J. S.

Argine and Arginine. By ANASTASIO QUIROGA (*Bull. Soc. Chim.*, 1897, [iii], **15**, 787—791).—The author uses the name arginine for an alkaloid obtained from a tree which he terms argine, one of a class called by the natives of Paraguay *viraró-mi*. The alkaloid forms prismatic crystals, is not altered in air or on exposure to light, and is soluble in alcohol, chloroform, or benzene, but only sparingly so in ether, light petroleum, or water. Its reaction with the ordinary alkaloidal reagents are described. M. W. T.

NOTE.—This new alkaloid would be better named *argine*, the name "arginine" being already applied to a well-known base.—EDITORS.

Organic Chemistry.

American Petroleum. By Charles F. Mabery and Arthur S. Kittelberger (*Amer. Chem. J.*, 1897, 19, 374—381).—A sample of petroleum, collected near the Magdalena River in the United States of Colombia, S. America, was found to consist practically of a single series of hydrocarbons, very possibly C_nH_{2n}; not more than a trace of aromatic hydrocarbons was present. The crude oil was dark in colour, thick, and viscous; it had sp. gr. = 0·9480 at 20°, absorbed bromine equivalent to 12·09 per cent., and contained ash 0·011, sulphur 0·68, nitrogen 0·318, carbon 85·63, and hydrogen 11·90 per cent.

A sample of petroleum from Oregon also contained but a trace of aromatic hydrocarbons, and had a composition intermediate between those required by the series C_nH_{2n+2} and C_nH_{2n-6}. The crude oil was thick and dark, had sp. gr. = 0·9597 at 20°, and contained sulphur 1·19, nitrogen 0·868, carbon 86·06, and hydrogen 11·87 per cent.

C. F. B.

Constituents of Petroleum between 150° and 220°. By Charles F. Mabery (*Amer. Chem. J.*, 1897, 19, 419—482).—On account of the conflicting statements and erroneous assumptions concerning the composition of Pennsylvanian petroleum boiling above 150°, based on Markownikoff's results on Russian oil, the author has further studied this, as well as Ohio and Canadian petroleums. The two principal objects in view were (*a*) to determine the nature of the series of hydrocarbons which form the main body of American petroleum, and (*b*) to ascertain whether the composition of Pennsylvanian, Ohio, and Canadian petroleums is, as regards their principal constituents, the same.

Generally speaking, the separation of the constituents with higher boiling point presents greater difficulties than of those in the portions boiling below 150°. In the latter case, there is no danger of decomposition, which is, however, met with in the former, on account of the presence of unstable substances such as nitrogen, oxygen, and sulphur compounds. The difficulty may be overcome by distillation in a vacuum, but the hydrocarbons separated in this manner may before purification be contaminated by other substances whose boiling points are nearly the same.

As it was found that cracking in refining does not begin to any considerable extent below 225°, refinery distillates were generally used, especially from Pennsylvanian oil. Most of the results on Ohio and Canadian oils were obtained from vacuum distillates, the preparation of which has been previously described (*Amer. Chem. J.*, 17, 713).

Pennsylvanian Petroleum.—As a result of this examination, it may be stated that the constituents with boiling points 163—164°, 173—174°, 196—197°, and 215—216° constitute the main body of this petroleum within these limits, and that they are members of the hydrocarbon series C_nH_{2n+2}. Any other substances present are found only in comparatively small quantities. No direct estimation can be based on these observations as to the proportion of aromatic hydrocarbons present, but among those identified may be mentioned mesitylene, cumene, pseudocumene, cymene, isocymene, durene, and isodurene.

For the separation of the hydrocarbons, refinery distillate at 48—50° Baumé, specific gravity 0·7892 at 20°, was used. It was nearly colourless, and gave no odour of decomposition.

Decane, $C_{10}H_{22}$, 163—164°.—The fraction of the crude oil 150—170° was carried through a long series of distillations until a large amount collected between 158—162° at 730 mm., and finally 162—163° at 760 mm. A portion of the oil, after being dried over sodium, being still impure, was purified by treatment with a mixture of nitric and sulphuric acids, which caused the separation of a considerable amount of solid material, which, by its melting point, &c., was shown to consist of dinitromesitylene. After this treatment, the oil gave on analysis correct numbers for $C_{10}H_{22}$, had sp. gr. 0·7479 at 20°, and vapour density = 4·91 (calc. 4·91). That this substance is a decane is further shown by a determination of its molecular weight by the Beckmann method, which gave 142 (calc. 142).

On subjecting the purified hydrocarbon to the action of chlorine in sunlight, a *monochlorodecane* boiling at 125—130° at 80 mm., and also a *dichlorodecane* boiling at 160—170°, were obtained.

Decane, $C_{10}H_{22}$, 173—174°.—On treating the crude distillate 169—170° with nitric and sulphuric acids, a nitro-derivative of cymene was separated. The purified hydrocarbon boils at 173—174°, has a sp. gr. 0·7467 and molecular weight, as determined by Beckmann's method, of 144; and, on chlorination, two products were obtained, a monochlorodecane boiling at 130—140° in a vacuum, and a dichlorodecane boiling at 170—171° at 80 mm.

Hendecane, $C_{11}H_{24}$, 196°, was isolated from the fraction 189—192°, which on nitration deposits a heavy nitro-compound, sparingly soluble in hot alcohol, from which solvent it crystallises in needles melting at 169—170°; the amount of the product was unfortunately insufficient for complete identification. The purified hydrocarbon boils at 196—197° at 760 mm., has sp. gr. 0·7581 and molecular weight 157 (calc. 156). By chlorination, *monochlorohendecane* boiling at 145—150° at 80 mm., and 225—230° at 747 mm., and a *dichlorohendecane* boiling at 190—200° in a vacuum, were obtained. A molecular weight determination of the monochloro-derivative gave 191, which agrees with the calculated 190.

Dodecane, $C_{12}H_{26}$, 214—216°, was obtained from the fraction of crude oil boiling between 208—210° at 730 mm. The pure substance has sp. gr. = 0·7729 and molecular weight 173 (calc. 170). It yielded a monochloro-derivative boiling at 142—153° at 20 mm., and at 230—235° under ordinary atmospheric pressure.

Ohio Petroleum.—By similar experimental data, the author shows that the composition of Ohio Trenton limestone petroleum, as regards the members of the series C_nH_{2n+2}, is identical with that of Pennsylvanian petroleum within the same limits of temperature, but a larger proportion of aromatic hydrocarbons is present.

Canadian Petroleum.—The constituents of Canadian corniferous limestone petroleum are also the same at 163° and 173°, but the hydrocarbons collecting at 196° and 214° have a composition represented by the general formula C_nH_{2n}. The proportion of aromatic hydrocarbons is greater than in either Ohio or Pennsylvanian petroleum. There are also indications that the heavier constituents contain other substances than the aromatic hydrocarbons, but for their complete identification very large amounts of liquid would have to be dealt with.

With Canadian petroleum, it is necessary that even the earlier distillations should be done in a vacuum, not only on account of the greater quantity of sulphur compounds, but also on account of the greater proportion of unsaturated hydrocarbons and the smaller proportion of the members in question that distil between 160° and 216°. When first distilled, the fractions are colourless, but on standing they become coloured, due to the polymerisation of the unsaturated hydrocarbons, for after the removal of these bodies the oils remain colourless. The greater specific gravity of these fractions is due to aromatic constituents, and it appears probable that naphthenes are present in small amount.

Hydrocarbon, $C_{11}H_{22}$.—The portions of crude oil boiling between 188—200° were repeatedly fractionated until the largest portion came together at 196—197°. On treatment with nitric and sulphuric acids, a small amount of a nitro-compound, crystallising from alcohol and melting at 150—154°, was obtained; this melting point is near to that of dinitroisodurene (156°). After thrice repeating the purification, the oil, on analysis, gave numbers agreeing with those required for $C_{11}H_{22}$; it had a sp. gr. = 0·7729, and a molecular weight of 154 (calc. 154). The classification of this hydrocarbon is difficult; it is not an unsaturated member of the ethylene series, because it lacks additive power for the halogens, &c., and its specific gravity is much less than that of the naphthene that Markownikoff and Ogloblin separated from Russian oil at 196—197°. The substance gives a monochloro-derivative of the formula $C_{11}H_{21}Cl$, which distils at 220—228° under atmospheric pressure.

Hydrocarbon, $C_{12}H_{24}$, was obtained after repeated treatment with fuming sulphuric acid of the crude oil boiling between 208—212°. It boils at 212—214° at 745 mm., has sp. gr. = 0·7857, and gives a monochloro-derivative boiling at 160—170° in a vacuum, as well as a small amount of what appears to be a dichloro-derivative. A. W. C.

Refractive Power of Hydrocarbons [from Petroleum] and their Chlorine Derivatives. By Charles F. Mabery and Edward J. Hudson (*Amer. Chem. J.*, 1897, **19**, 482—485).—The authors have determined the refractive power of the hydrocarbons and their chlorine derivatives mentioned in the preceding abstract. A gradual increase in refractive power is noticed with increase in boiling point, which becomes more regular after purification of the distillates. Higher values are obtained from Ohio and Canadian distillates than from

Pennsylvanian oil, analogous to the differences in specific gravity alluded to.

The quantities of the chlorine derivatives were too small to allow of complete purification, but there is a well-marked difference between the refractive power of the hydrocarbons and their monochloro-derivatives, as also between the monochloro- and dichloro-derivatives, showing the influence of the chlorine atoms. A. W. C.

Action of Alcoholic Potash on Dihalogen Derivatives. By IDA WELT (*Ber.*, 1897, **30**, 1493—1496. Compare Krafft, Abstr., 1896, i, 665).—In continuation of Krafft's work, the author has undertaken the study of the action of alcoholic potash on hexylenic bromide and heptylenic bromide, the hexylenic bromide, boiling at 78° under a pressure of 12 mm., being obtained by the addition of bromine to hexylene from β-hexylic iodide. When this bromide is boiled for 12—15 hours with its own weight of potassium hydroxide dissolved in alcohol, or heated with it in a soda-water bottle for 5—6 hours at 70°, two products are always obtained; these are easily separated by fractional distillation in an atmosphere of carbonic anhydride, the more volatile product being butylacetylene boiling at 70·5—72°; and the less volatile a monobromhexylene boiling at 46° under 20 mm. pressure. The latter, when heated at 110° for 14 hours with its own weight of potash not completely dissolved in alcohol, yields methylpropylacetylene boiling at 83°. From these facts, the author concludes that hexylene obtained from β-hexylic iodide consists, at least to a large extent, of normal hexylene, $CH_3\cdot[CH_2]_4\cdot CH\colon CH_2$. Good yields of heptylene cannot be obtained by the action of alcoholic potash on normal heptylic bromide or iodide, the chief product in both cases being ethylic heptylic ether, $C_7H_5\cdot O\cdot C_2H_5$. The best method of obtaining normal heptylene is by Krafft's method (Abstr., 1884, 571). Pure heptylic palmitate is heated in an atmosphere of carbonic anhydride at 350°, when it is decomposed into heptylene which distils over and free palmitic acid. Heptylene boils at 95° and yields a dibromide boiling at 105—107° under a pressure of 15 mm. When the dibromide is heated at 70° for several hours with its own weight of potassium hydroxide not completely dissolved in alcohol, it yields heptinene (normal amylacetylene), $C_5H_{11}\cdot C\vdots CH$, boiling at 100—101°, and also a considerable quantity of unaltered monobromheptylene which is only slowly acted on when heated to higher temperatures with alcoholic potash. The author also confirms Limpricht's experiments on œnanthylidene chloride; this compound, when heated with alcoholic potash, yields normal amylacetylene and a chlorœnanthylene, $C_7H_{13}Cl$, boiling at 148°. J. J. S.

Molecular Weight of Ethylic Ferrocyanide. By GUSTAV BUCHBÖCK (*Zeit. physikal. Chem.*, 1897, **23**, 157—158).—The author determined, by the cryoscopic method, the molecular weight of ethylic ferrocyanide, a compound which dissolves readily in water without dissociation.

The values obtained varied from 316 to 333, that corresponding with the formula $(C_2H_5)_4Fe(CN)_6$ being 328, so that the ferrocyanides are represented by the simplest formula. L. M. J.

Ethereal Salts of Secondary Allylic Alcohols. By H. FOURNIER (*Bull. Soc. Chim.*, 1897, [iii], 15, 884—889).—The following salts were prepared from ethylallylcarbinol; the acetate has already been described (Abstr., 1895, i, 198). *Ethylallylcarbinylic propionate*, obtained by the action of propionic chloride, is a colourless liquid boiling at 168—170°, and of sp. gr. 0·884 at 18°. The *isovalerate*, obtained by heating with isovaleric anhydride at 130°, is a colourless liquid boiling at 196—198°, and of sp. gr. = 0·873 at 18°. The *benzoate* is a colourless liquid boiling at 190—192° under 110 mm. pressure, or at 259—260° under atmospheric pressure, and of sp. gr. = 0·990 at 20°. The *chloride*, obtained by the action of phosphorus pentachloride, is a colourless liquid boiling and decomposing between 120° and 123°.

The following salts were prepared from isopropylallylcarbinol. The *acetate*, already described (*loc. cit.*). The *propionate*, by the action of propionic chloride, is a colourless liquid boiling at 178—180°, and of sp. gr. = 0·882 at 18°. The *isovalerate* is a colourless liquid boiling at 205—207°, and of sp. gr. = 0·870 at 18°. The *chloride*, by the action of phosphorus pentachloride, is a colourless liquid boiling with decomposition between 125 and 130°. The *sulphate*, $CH(C_3H_7)(C_3H_5)\cdot SO_4H$, is produced by the action of the alcohol on excess of sulphuric acid at −15°. Its barium salt, which crystallises with 5 molecules of water, is a white and extremely deliquescent substance.

The following salts were prepared from isobutylallylcarbinol. The *acetate*, already described (*loc. cit.*). The *propionate*, a colourless liquid, boiling at 195—197°, and of sp. gr. 0·874 at 18°. The *isovalerate*, a colourless liquid boiling at 220—222°, and of sp. gr. 0·867 at 18°. The *benzoate*, a colourless liquid boiling at 208—211° under 110 mm. pressure and 274—277° at 760 mm., and of sp. gr. 0·966 at 20°. The *chloride*, already described (this vol., i, 233), and the *sulphate*, $CH(C_4H_9)(C_3H_5)\cdot SO_4H$; its barium salt, after standing in a desiccator for 2 months, retained 2 molecules of water. M. W. T.

Reduction of Tertiary Nitroisobutylglycerol [Nitrotrihydroxy-tert.-butane] and Dihydroxyacetoxime. By OSKAR PILOTY and OTTO RUFF (*Ber.*, 1897, 30, 1656—1665).—When tertiary nitrotrihydroxybutane (*Compt. rend.*, 121, 210) (10 grams) and crystallised aluminium sulphate (45 grams) are dissolved in water (300 grams), and then, while the solution is constantly stirred, gradually treated with 2½ per cent. sodium amalgam (360 grams), the chief reduction product is tertiary *hydroxylaminotrihydroxybutane* (2-methylol-2-hydroxylaminopropandiol-1 : 3), $OH\cdot NH\cdot C(CH_2\cdot OH)_3$. After careful purification (for which see original), this compound forms colourless crystals melting at 140° (corr.). It is readily soluble in water, moderately in methylic alcohol, somewhat sparingly in warm ethylic alcohol or in acetone, and practically insoluble in ether. It turns turmeric paper brown, red litmus paper blue, and also reacts with phenolphthalein; it possesses a somewhat sweet taste, and reduces Fehling's solution in the cold. The only crystalline salt which could be obtained was the *oxalate*, $[OH\cdot NH\cdot C(CH_2\cdot OH)_3]_2,H_2C_2O_4$, which crystallises in plates, and melts and decomposes at 141°, is readily soluble in water, but only sparingly soluble in methylic or ethylic alcohol. The *picrate* melts at 113—114° (corr.). The hydroxylamino-compound, when treated with sodium nitrite and hydrochloric acid, yields the *nitroso*-derivative, $OH\cdot N(NO)\cdot C(CH_2\cdot OH)_3$, melting and decomposing at 147°. It is readily soluble in water, also in methylic or warm ethylic alcohol, and does not reduce Fehling's solution even on warming; the nitroso-compound is relatively stable, but is completely decomposed when boiled with dilute acids. The *lead* salt decomposing at about 195°, and the *methylic* ether, $OMe\cdot N(NO)\cdot C(CH_2\cdot OH)_3$, melting at 158—160° (corr.), are both described. No crystalline products could be obtained on reducing the nitroso-compound with sodium amalgam and alcohol.

When an alcoholic solution of tertiary hydroxylaminotrihydroxybutane is continuously shaken and treated at the same time with small quantities of mercuric oxide until the latter is no longer reduced, a strong odour of formaldehyde is developed, and the clear solution, after evaporating under reduced pressure yields crystals of *dihydroxyacetoxime*, $OH\cdot N\colon C(CH_2\cdot OH)_2$. It crystallises from alcohol in pointed pyramids, melts at 84° (corr.), and is readily soluble in water or methylic alcohol, but extremely sparingly in ether. Treated with an excess of phenylhydrazine, the oxime yields the osazone previously obtained by Fischer and Tafel (Abstr., 1888, 1264) from glycerose. The authors have also been able to obtain the same oxime directly from glycerose. The oxime, when reduced according to Goldschmidt's method (Abstr., 1887, 249), yields as the chief product isopropylamine; by reducing with sodium amalgam and aluminium sulphate the corresponding *amine*, $NH_2\cdot CH(CH_2\cdot OH)_2$, was obtained in the form of its *sulphate*. This salt is extremely hygroscopic, but the *hydrochloride* is less so, and melts at 95—97°.
J. J. S.

Remarkable Behaviour of Chloral Hydrate with Starch and Iodine. By EDUARD SCHÄR (*Chem. Centr.*, 1896, ii, 661; from *Pharm. Centr. H.*, **37**, 540—542).—By shaking 1 part of palm-sago starch with 1000 parts of chloral hydrate solution (10 parts of water to 7 parts of chloral hydrate) an almost clear, viscous solution is obtained which, after prolonged standing, or filtering by suction, does not give a blue coloration on addition of solid iodine or of a solution of iodine in chloral hydrate. An unfiltered solution, or one simply decanted off the sediment and containing small quantities of undissolved starch grains, gives the blue coloration on addition of iodine. On adding powdered iodine and concentrated chloral hydrate solution to pure sago-starch under similar conditions, a deep blue solution is quickly formed which rapidly becomes viscous, and contains gelatinised starch and the iodine-starch compound. If an excess of the solution of iodine in chloral hydrate is added, the iodine-starch compound separates as a deep blue, powdery sediment, and there is no perceptible swelling or solution of the starch grains. On pouring two to three times the volume of water on to the reddish-brown solution, prepared by allowing a solution of starch in chloral hydrate to stand over solid iodine, the blue coloration begins to develop at the zone of contact, and gradually spreads throughout the whole liquid. The starch undergoes no change, hence excess of chloral hydrate apparently exercises a curious retarding influence under certain conditions on the production of the blue iodine-starch compound. E. W. W.

Action of Chloroform on Starch. By Franz Musset (*Chem. Centr.*, 1896, ii, 703—704; from *Pharm. Centr. H.*, **37**, 587—588).—If a solution of starch in zinc chloride to which chloroform has been added is allowed to stand 3 months, the whole of the starch is converted into dextrin, and the solution does not give the iodine coloration, but, on adding iodine and shaking, the iodine is dissolved by the chloroform. The iodine-starch compound is not decomposed by chloroform, but all the iodine-dextrin compounds lose their iodine on shaking with chloroform, but with greater difficulty the less the content of iodine, so that a dextrin solution withdraws iodine from a strong solution of iodine in chloroform. In this slow conversion of starch into dextrin, intermediate products are formed. On evaporating the zinc chloride solution containing chloroform and adding three times its volume of alcohol, the dextrins separate. By dissolving the precipitate, after the lapse of 48 hours, in water with addition of a drop of hydrochloric acid, again precipitating with alcohol and repeating the process twice to remove the zinc chloride, a dextrin is obtained which is insoluble in cold water but dissolves in hot. The residue obtained by evaporating the solution is not more soluble in cold water, and gives a blue coloration with iodine. The filtrate from this dextrin, after evaporation on the water bath and treatment of the residue with cold water, yields a second insoluble dextrin the properties of which are similar to those of the first. The aqueous filtrate from the second dextrin contains a dextrin resulting from the action of boiling zinc chloride and chloroform, which cannot be isolated.

Chloroform converts starch-paste into a soluble modification similar to that obtained by the action of hydrochloric acid, and on heating a mixture which has stood some months, the starch dissolves and separates as a fine paste on cooling. E. W. W.

Compound of Silver Chloride and Methylamine. By R. Jarry (*Compt. rend.*, 1897, **124**, 963—965).—Silver chloride dissolves readily in liquid methylamine prepared from the carefully purified hydrochloride, and the syrupy solution, when evaporated, yields birefractive crystals of a compound $AgCl,NH_2Me$. The same compound is formed by the action of gaseous methylamine on silver chloride at the ordinary temperature. Its dissociation pressures are as follows:

T.	0°	16·8°	20·5°	32°	41°	51°	61°	65°
Pressure	9	32	43	92	168	312	584	755 mm.

The solubility of silver chloride in an aqueous solution of methylamine varies with the temperature, and a solution saturated at 20° deposits birefractive crystals which are not silver chloride. The author is investigating the conditions under which the methylamine and silver chloride combine and dissociate. C. H. B.

Correction [Ethanolamines]. By Ludwig Knorr (*Ber.*, 1897, **30**, 1492. Compare this vol., i, 313, 314).—The author corrects the numbers previously given for the molecular dispersions of the three ethanolamines. The correct figures are ethanolamine (amidoethylic alcohol), 0·41; diethanolamine, 0·67; triethanolamine, 1·07.

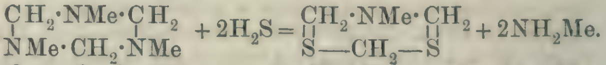
J. J. S.

Methylguanidine. By N. A. Orloff (*Chem. Centr.*, 1896, ii, 662; from *Pharm. Zeit. Russ.*, 35, 513—514).—This compound, which Brieger has obtained as a ptomaine from putrefying meat, is prepared from the creatinine of urine, as follows. The urine, to which sodium acetate has been added, is precipitated by mercuric chloride solution and the washed precipitate boiled with water, calcium hydroxide, and freshly precipitated mercuric oxide in order to oxidise the creatinine to methylguanidine and oxalic acid. By saturating the solution with picric acid, concentrating and leaving it for some time, long, silky, yellow crystals of methylguanidine picrate are obtained, and may be split into their components by recrystallisation from hot water and treatment with lead hydroxide or quinine.

This method serves also as a good test for the presence of creatinine in urine.

E. W. W.

Action of Hydrogen Sulphide on Trimethyltrimethylenetriamine. By Marcel Delépine (*Bull Soc. Chim.*, 1897, [iii], 15, 889—891).—When hydrogen sulphide is passed into trimethyltrimethylenetriamine, the liquid separates into two layers. The upper layer, which remains liquid and is soluble in water, consists of methylamine hydrosulphide; the lower layer, which solidifies, is thialdine, a white, crystalline substance which has been described by Wohl. The reaction may be represented by the equation:



$$\begin{array}{l}CH_2{\cdot}NMe{\cdot}CH_2\\ |\qquad\qquad\quad |\\ NMe{\cdot}CH_2{\cdot}NMe\end{array} + 2H_2S = \begin{array}{l}CH_2{\cdot}NMe{\cdot}CH_2\\ \|\qquad\qquad\quad \|\\ S\!-\!\!-\!CH_2\!-\!\!-\!S\end{array} + 2NH_2Me.$$

This confirms the formula given by Wohl, on one hand, and by Brochet and Cambier (Abstr., 1895, i, 641), on the other, to thialdine and trimethyltrimethylenetriamine.

M. W. T.

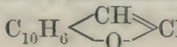
Action of Carbon Bisulphide on Trimethyltrimethylenetriamine. By Marcel Delépine (*Bull. Soc. Chim.*, 1897, [iii], 15, 891—899).—*Dimethylformocarbothialdine.*—Carbon bisulphide reacts with trimethyltrimethylenetriamine with development of heat, forming a compound soluble in alcohol and melting at 96° which is isomeric with carbothialdine, produced by the action of carbon bisulphide on aldehyde-ammonia. Its constitution is represented by the formula $CS_2(CH_2NMe)_2$; in presence of hydrochloric acid, it breaks up into carbon bisulphide, formaldehyde, and methylamine. If an alcoholic solution is used, diethylic methylenic ether is formed. This substance, together with methylamine hydriodide and the hydriodide of a base, $C_4H_9NS_2$, is produced by the action of methylic iodide on a solution of dimethylformocarbothialdine in alcohol.

Dimethylic methylimidothiocarbonate, $NMe{:}C(SMe)_2$, is produced from the iodide mentioned above. It is a liquid heavier than water, in which it is insoluble; it is very soluble in organic solvents and boils without decomposition at 192°. The hydriodide is very soluble in water and somewhat soluble in alcohol. It melts at 142°.

The constitution of this substance is discussed at some length.

M. W. T.

Diethylformocarbothialdine. By Marcel Delépine (*Bull. Soc. Chim.*, 1897, [iii], 15, 899—900).—By the action of carbon bisulphide on the compound $CH_2{:}NEt$, or its polymeride, $(CH_2{:}NEt)_3$, diethylformocarbothialdine, $CS_2,2CH_2{:}NEt$, is produced. It melts at 55°, and reacts with methylic iodide to yield dimethylethylimidothiocarbonate, which boils at 200°. M. W. T.

Derivatives of Acetal. By Julius Hesse (*Ber.*, 1897, 30, 1438—1442).—When α-naphthol is heated with alcoholic potash and chloracetal, it yields *α-naphthofurfuran*,  $C_{10}H_6{<}\begin{smallmatrix}CH\\O\end{smallmatrix}{>}CH$, which melts at 59° and boils at 288° (uncorr.). The *β-compound* melts at 65° and boils at 280° (uncorr.). When a solution of sodium in alcohol is employed instead of alcoholic potash, however, a naphthoxyacetal is produced. *β-Naphthoxyacetal*, $C_{10}H_7{\cdot}O{\cdot}CH_2{\cdot}CH(OEt)_2$, boils at 240° (pressure = 60 mm.) and is slightly volatile with steam. *Paratolyloxyacetal*, $C_7H_7{\cdot}O{\cdot}CH_2{\cdot}CH(OEt)_2$, is formed both with sodium ethoxide and alcoholic potash and boils at 262—263° (uncorr.). When boiled with water, it yields *paratolyloxyacetaldehyde hydrate*, which crystallises in slender, white needles melting at 65°. The corresponding *aldehyde* is a thick liquid, distilling at about 150°, which yields a *phenylhydrazone*, melting at 106°. *Paratolyloxyacetaldoxime* crystallises from alcohol in rhombic tablets melting at 68°. The hydrate is converted by digestion with silver oxide into paratolyloxyacetic acid.

Metatolyloxyacetal boils at 262—263° (uncorr.); the *aldehyde hydrate* melts at 56°. The *phenylhydrazone* melts at 72° and the *oxime* at 82°.

Moniodo-acetal is obtained by the action of iodine and iodic acid on acetal, and is a colourless liquid of sp. gr. 1·4944 at 15°, and boils at 100° (pressure = 70 mm.), but decomposes at higher pressures. It was not found possible to replace the halogen atom of this compound, or of chloracetal, by the cyanogen group. A. H.

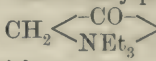
Disubstituted Amidoacetal and the Preparation of Homologues of Betaine and Choline. By Richard Stoermer and Friedrich Prall (*Ber.*, 1897, 30, 1504—1514).—In this research, the tertiary acetal bases were prepared partly from the secondary amines and chloracetal, and partly by the Hofmann reaction from the alkylammonium hydroxides; by converting the halogen alkyl additive products of the acetal bases into the corresponding aldehydes and oxidising with silver oxide, homologues of betaine were produced, whilst on reduction with sodium amalgam higher cholines were formed.

Diethylamidoacetal, $NEt_2{\cdot}CH_2{\cdot}CH(OEt)_2$, from monochloracetal and diethylamine, boils at 194—195°, and its *hydrochloride* is extremely deliquescent; the hydrochloride of *diethylamidoacetaldehyde*,

$$NEt_2{\cdot}CH_2{\cdot}CHO,HCl,$$

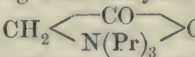
is formed from the acetal on treating it with hydrochloric acid by E. Fischer's method. It takes up water readily from moist air and melts at 111—112°; the *aurochloride* melts at 96°, the *platinochloride* at 156°, and the *picrate* at 104°.

Methylethylamidoacetal, $NMeEt\cdot CH_2\cdot CH(OEt)_2$, prepared through the ammonium hydroxide, is a colourless, mobile liquid boiling at 179—180° and yielding a yellow *aurochloride* melting at 61°, and a fine, yellow *picrate* melting at 89°.

Triethylacetaldehydeammonium chloride, $NEt_3Cl\cdot CH_2\cdot CHO$, obtained from the ethiodide of diethylamidoacetal (m. p. 78°) by the action of freshly precipitated silver chloride, consists of reddish-yellow crystals melting at 87—88°, and giving a bright yellow, crystalline *aurochloride* melting at 140°, a *platinochloride* decomposing at 198° and crystallising with $2H_2O$, and a yellow *picrate* melting at 204°. On treating this ammonium chloride with freshly precipitated silver oxide, *ethylbetaine* or *triethylglycocine*,  $CH_2{<}\begin{matrix}CO\\NEt_3\end{matrix}{>}O$, is produced; this forms delicate, white crystals which are extremely deliquescent; the *aurochloride* crystallises in large, yellow needles melting at 211—212°, and the *platinochloride* in thick, orange-yellow needles containing $4H_2O$ and melting at 110—112°; when dehydrated it, melts and decomposes at 205—206°. *Ethylchloline hydrochloride*,

$$OH\cdot CH_2\cdot CH_2\cdot NEt_3Cl,$$

is obtained from the compound above-mentioned on reduction with sodium amalgam in acid solution; it yields a *platinochloride* melting and decomposing between 212° and 216°.

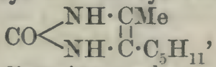
Dipropylamidoacetal, $NPr_2\cdot CH_2\cdot CH(OEt)_2$, prepared as above, is a colourless liquid boiling at 223°, the *hydrochloride* of which cannot be obtained in a crystalline condition; the *aurochloride* is an oil, the *methiodide* forms yellowish-white crystals melting at 79—80°; the *hydrochloride* of *dipropylamidoacetaldehyde*, $NPr_2\cdot CH_2\cdot CHO,HCl$, melts at 111—112°, and forms an *aurochloride* melting at 73—74°, a *platinochloride* melting at 86°, and a *semicarbazone* crystallising from ether in white crystals melting at 147°; *tripropylacetaldehydeammonium chloride*, $NClPr_3\cdot CH_2\cdot CHO$, forms feather-like crystals melting at 95—96°, and yields an *aurochloride* melting at 135°, and a *platinochloride* melting and decomposing when anhydrous at 180—183°; *propylbetaine* or *tripropylglycocine*,  $CH_2{<}\begin{matrix}CO\\N(Pr)_3\end{matrix}{>}O$, crystallises in slender, white needles melting at 184°, and yields an *aurochloride* melting at 116°, and a *platinochloride*, with $2H_2O$, melting at 90—95°.

Methylpropylamidoacetal, $NMePr\cdot CH_2\cdot CH(OEt)_2$, boils at 193—195°, its *aurochloride* melts at 38—39° and the *picrate* at 93°; the *methiodide* consists of very deliquescent, quadratic prisms.

Dimethylamidoacetal, $NMe_2\cdot CH_2\cdot CH(OEt)_2$, boils at 170—171°, and yields an *aurochloride* melting at 78—79°, a *platinochloride* melting at 92°, and a *picrate* melting at 80°; *dimethylamidoacetaldehyde*,

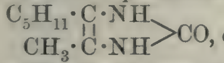
$$NMe_2\cdot CH_2\cdot CHO,$$

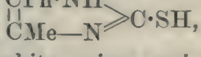
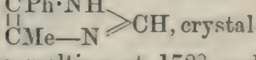
a brownish oil, forms a crystalline *platinochloride* melting at 121—122° and a *picrate* melting at 96°. J. F. T.

Some Amidoketones. By L. Behr-Bregowski (*Ber.*, 1897, **30**, 1515—1525).—*Methyl amidohexyl ketone*, $C_5H_{11}\cdot CH(NH_2)\cdot CO\cdot CH_3$, which is best prepared from methyl isonitrosohexyl ketone, yields a *hydrochloride* crystallising in fine, white needles melting at 110—112°, and a *picrate* melting at 80—85°; with potassium thiocyanate, the hydrochloride yields *αβ- or βα-methylamylimidazolyl mercaptan*, forming white, microscopic needles melting at 224°, and this, on oxidation, gives the *αβ- or βα-methylamylimidazole*, $C_3N_2HMe\cdot C_5H_{11}$. The latter yields a crystalline *platinochloride* melting and decomposing after recrystallisation from alcohol at 181—183°, and an *aurochloride* melting at 137—138°; the *free base* could not be obtained in the crystalline condition. Potassium cyanate reacts with methyl amidohexyl ketone hydrochloride, forming *methylamylimidazolone*,  $CO<\begin{array}{l}NH\cdot CMe\\ \quad\ \ \| \\ NH\cdot C\cdot C_5H_{11}\end{array}$, which crystallises from dilute alcohol in white, glistening scales melting and decomposing at 243°. Methyl amidohexyl ketone, on oxidation with mercuric chloride, yields *dimethyldiamylpyrazine*, $C_4N_2Me_2(C_5H_{11})_2$; this forms a *platinochloride* crystallising from alcohol in yellow, rhombohedra melting at 225—231°.

In the same way, *isoamylisonitrosoacetone*,

$$CHMe_2\cdot CH_2\cdot CH_2\cdot C(NOH)\cdot CO\cdot CH_3,$$

a yellow solid of low melting point, yields, on reduction, *isoamylamidoacetone*, $C_5H_{11}\cdot CH(NH_2)\cdot CO\cdot CH_3$, which separates from its alcohol solution in small, white needles melting at 123—125°; it yields a *picrate* melting at 128—129°. With potassium thiocyanate, the hydrochloride of the base yields *αβ- or βα-methylisoamylimidazolyl mercaptan*, $\begin{array}{l}C_5H_{11}\cdot C—N\\ \qquad\ \ \|\\ \ \ CH_3\cdot C\cdot NH\end{array}>C\cdot SH$, or $\begin{array}{l}C_5H_{11}\cdot C\cdot NH\\ \qquad\ \ \|\\ \ \ CH_3\cdot C—N\end{array}>C\cdot SH$, forming red crystals melting and decomposing at 255°; whilst, on oxidation, it is converted into *αβ- or βα-methylisoamylimidazole*. This crystallises in small, white quadratic prisms melting at 131—132°; the *aurochloride* melts at 156°, and the *platinochloride* at 191—192°. *Methylisoamylimidazolone*,  $\begin{array}{l}C_5H_{11}\cdot C\cdot NH\\ \qquad\ \ \|\\ \ \ CH_3\cdot C\cdot NH\end{array}>CO$, crystallises from alcohol in long, glistening needles melting and decomposing at 271°.

Phenyl amidoethyl ketone, $NH_2\cdot CH_2\cdot CH_2\cdot CO\cdot C_6H_5$, obtained from phenyl isonitrosoethyl ketone by reduction, separates from concentrated hydrochloric acid in large, white crystals melting at 223—225°, the *hydrochloride* forms microscopic needles which melt at 183—184°, the *platinochloride*, red prisms melting at 195—200°, and the *picrate* yellow needles melting at 160; with potassium thiocyanate, it yields *αβ- or βα-phenylmethylimidazolyl mercaptan*,  $\begin{array}{l}CPh\cdot NH\\ \|\\ CMe—N\end{array}>C\cdot SH$, a substance crystallising from dilute alcohol in white, microscopic prisms, melting at about 300°. *Phenylmethylimidazole*,  $\begin{array}{l}CPh\cdot NH\\ \|\\ CMe—N\end{array}>CH$, crystallises from ether in yellow, transparent plates melting at 178°, and yielding a *platinochloride* melting at 214—215°, an *aurochloride* melting at 188—190°, and a *picrate* which forms fine, yellow needles melting at 196°; *phenylmethylimidazolone*, $\begin{array}{l}CPh\cdot NH\\ \|\\ CMe\cdot NH\end{array}>CO$, from the ketone and potassium cyanate, forms glistening leaflets melting at 285—286°; *phenyl benzamidoethyl ketone*, C_6H_5·CO·CHMe·NHBz, is obtained from the amidoketone and benzoic chloride; it crystallises from dilute alcohol in well-formed rhombohedra melting at 103°. On reduction, it gives *phenylbenzamidoethylcarbinol*, OH·CHPh·CHMe·NHBz, a substance crystallising from 80 per cent. alcohol in small, white needles melting at 136—138°. J. F. T.

Cerotic Acids and Cerylic Alcohol. By ROBERT HENRIQUES (*Ber.*, 1897, **30**, 1415—1418).—Chinese wax is produced on the Chinese ash (*Fraxinus Chinensis*) by *Coccus ceriferus* (Fabr.), and consists for the most part of cerylic cerotate (Brodie, *Annalen*, 1848, **67**, 199); the author's investigation of this substance points to the formula $C_{52}H_{104}O_2$ as representing the composition, and he regards cerotic acid and cerylic alcohol as having the formulæ $C_{26}H_{52}O_2$ and $C_{26}H_{54}O$ respectively. Brodie's formulæ are $C_{27}H_{54}O_2$ and $C_{27}H_{56}O$, whilst T. Marie, who has prepared numerous compounds of this series (compare Abstr., 1896, i, 346, and this vol., i, 266), represents them by the expressions $C_{25}H_{50}O_2$, and $C_{25}H_{52}O$ respectively; the identity of the acids obtained from Chinese wax and from beeswax has not, however, been established absolutely. M. O. F.

The Benzylimides of Malic Acid. By ALBERT LADENBURG and W. HERZ (*Ber.*, 1897, **30**, 1582—1584. Compare this vol., i, 138.)—Two isomeric benzylmalimides have been described by Giustiniani (Abstr., 1892, 820), the α-modification being less soluble in water than the β-compound. Investigation of these substances from the point of view of optical rotation has led the authors to the conclusion that only one benzylimide of active malic acid exists, the so-called α-benzylmalimide being a mixture of the imide of the active acid, which is readily soluble in water, with the sparingly soluble imide of the inactive acid.
M. O. F.

New Method of preparing Mesotartaric Acid and the Imides. By G. MEISSNER (*Ber.*, 1897, **30**, 1574—1578).—Treatment with boiling alkali reduces the activity of tartaric acid, and the author has therefore studied the conditions under which this change reaches a maximum, and finds that when 100 grams of tartaric acid is heated with 350 grams of caustic soda (13 mols.) and 700 grams of water in a copper flask during 8 hours, the angle of rotation in a 10 per cent. solution drops to 0·05°; the product, however, is mainly racemic acid, the yield of mesotartaric acid amounting to only 1·3 per cent. Better results are obtained by Jungfleisch's method, which consists in heating tartaric acid (30 grams) with water (4 grams) in sealed tubes at 165—170°; controlling the temperature at 160—165°, the author has obtained 5·5 per cent. by this method.

The methylimide and ethylimide of mesotartaric acid have not been obtained; the hydrogen ethylamine salt loses water at 150—155°, and yields the ethylimide of racemic acid, which melts at 173° (compare this vol., i, 140). The hydrogen propylamine salt undergoes no change at 160°, but when heated with zinc chloride during 4 hours at 125° yields a product which may be the amido-acid $COOH\cdot CH(OH)\cdot CH(OH)\cdot CO\cdot NHPr$. The hydrogen benzylamine salt undergoes condensation when heated at 150—165°, yielding racemimide (m. p. 167°) and the *benzylimide* of mesotartaric acid, which crystallises from water in lustrous leaflets and melts at 123—126°. M. O. F.

α-Sulphocaproic Acid and its Salts. By BÉLA VON BITTÓ (*Ber.*, 1897, **30**, 1642—1648).—The author has obtained α-sulphocaproic acid by the action of ammonium sulphate on ethylic α-bromocaproate. The ethylic salt is heated with $2\frac{1}{2}$ times its weight of ammonium sulphate for 20 to 24 hours, and the small quantity of the ethylic bromocaproate which remains unacted on can be removed by extracting with ether; the aqueous solution, which contains the sulphonic acid in the form of its ammonium salt, is then boiled with lead oxide and the solution of the pure lead salt decomposed with sulphuric acid. In later experiments, it has been found more advantageous to isolate the acid by means of its barium and not of its lead salt. *α-Sulphocaproic acid*, $C_6H_{12}SO_5 + H_2O$, is a yellow syrup which, when kept over by sulphuric acid, solidifies to an indefinite crystalline mass. It gradually turns brown when kept, owing to the liberation of sulphuric acid. It is also readily decomposed when heated to 100°. The *ammonium hydrogen* salt, $C_6H_{11}SO_5NH_4 + H_2O$; *calcium* salt $(+1\frac{1}{2}H_2O)$, and *strontium* salt $(+\frac{1}{2}H_2O)$ are very fully described. The *zinc* salt $(+H_2O)$; *cadmium* salt $(+H_2O)$; and *silver* salt are also described.

J. J. S.

Action of Carbamide and Primary Amines on Maleic Anhydride. By FREDERICK L. DUNLAP and ISAAC K. PHELPS (*Amer. Chem. J.*, 1897, **19**, 492—496. Compare Abstr., 1896, i, 471).—*Maleinuric acid*, $NH_2\cdot CO\cdot NH\cdot CO\cdot CH\colon CH\cdot COOH$, is produced when maleic anhydride and carbamide in molecular proportion are heated at 100—105° in an oil bath. The crystals are perfectly white, and melt without decomposition at 167·5—168°. Although many attempts were made, the imide of maleic acid could not be obtained in quantities sufficient for complete identification by heating either maleinuric acid alone or a mixture of maleic anhydride and urea.

Paratolylmaleamic acid, $C_6H_4Me\cdot NH\cdot CO\cdot CH\colon CH\cdot COOH$, is formed when molecular proportions of maleic anhydride and paratoluidine are dissolved in chloroform and mixed; it crystallises from alcohol in lemon-yellow needles melting at 201°.

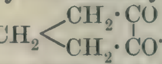
Orthotolylmaleamic acid, prepared in a similar manner, crystallises from alcohol in bunches of thick, light yellow prisms, melting at 117·5—118°.

β-Naphthylmaleamic acid crystallises from alcohol in bright yellow needles, which, when pure, melt and evolve gas at 200°. α-Naphthylamine appears to unite readily with maleic anhydride, but the product was not analysed. A. W. C.

Preparation of Zinc Ethyl. By ARTHUR LACHMANN (*Amer. Chem. J.*, 1897, **19**, 410—411).—A modification of the Gladstone and Tribe method (Trans., 1879, 750) was employed, the zinc-copper couple being used in the form of dust; the yield varied from 70 to 90 per cent. of the theoretical, with the sample of zinc dust used. To prepare the couple in this form, zinc dust is mixed with 12 per cent. of its weight of copper oxide, and the mixture heated in a combustion tube for 20 minutes to a dull red heat in a current of hydrogen. To prevent condensation of moisture and caking, the burners should be lighted under the whole length of the tube at once, and the nearer the temperature employed approaches the melting point of zinc the better; but, of course, the zinc must not be allowed to fuse. C. F. B.

The Hexamethylene Series. By NICOLAI D. ZELINSKY (*Ber.*, 1897, 1532—1540).—As the result of many experiments, the author concludes that it is possible to convert methylhexamethylene [methylcyclohexane] into dimethylpentamethylene by reducing the corresponding alcohol with hydriodic acid; if, however, the reduction be brought about by heating the bromide of β-methylhexamethylenic alcohol with zinc and hydrochloric acid, methylhexamethylene alone is formed.

J. F. T.

1:2-Diketopentamethylene (Cyclopentadione-1:2). By W. DIECKMANN (*Ber.*, 1897, **30**, 1470—1473).—When finely divided ethylic 1:2-diketopentamethylene-3:5-dicarboxylate (Abstr., 1894, i, 324) is boiled with dilute sulphuric acid, it is slowly converted by loss of carbonic anhydride into diketopentamethylene,  $CH_2<\begin{matrix}CH_2\cdot CO\\ \vert\\ CH_2\cdot CO\end{matrix}$. This, when distilled under a pressure of 20 mm. in an atmosphere of carbonic anhydride, passes over at 105°. It forms colourless crystals melting at 55°, and is extremely easily soluble in water, alcohol, ether, acetone, or chloroform, but only sparingly in carbon bisulphide or light petroleum. It resembles the 1:2-diketones of the fatty series in most of its chemical properties. It is remarkably stable towards acids, but alkalis readily convert it into a quinonic substance.

The *dioxime*, which melts and decomposes at about 210°, is but sparingly soluble in the usual organic solvents. The *osazone* crystallises in dark, purple crystals, and melts at 146°. The *monanil*, obtained by the action of aniline on a solution of the diketone in aqueous alcohol, melts at 111°. *Tribromodiketopentamethylene*, obtained by the action of bromine on a boiling solution of the diketone in carbon bisulphide, crystallises from light petroleum in colourless needles, and melts at 155°. J. J. S.

Semicarbazones of Cyclic Ketones. By NICOLAI D. ZELINSKY (*Ber.*, 1897, **30**, 1541—1544).—The semicarbazones of cyclic ketones, prepared in the usual way, are well-defined, crystalline substances. The semicarbazone of *ketohexamethylene* melts at 166—167°, of *β-methylketopentamethylene* at 184—185°, of *a-methylketohexamethylene* at 193—194° (with decomposition), of *β-methylketohexamethylene* Wallach) at 180—181°, of *β-methylketohexamethylene* (Einhorn) at 191—192°, of *γ-methylketohexamethylene* at 199°, of *ketoheptamethylene* (*suberone*) at 163—164°, of *aa-dimethylketopentamethylene* (I) at 190—191°, of *aa-dimethylketopentamethylene* (II) at 184—185° (with decomposition), of *γ-ethylketohexamethylene* at 175—176°, of *aa-dimethylketohexamethylene* (1) at 197—198° (with decomposition), of *aa-dimethylketohexamethylene*

(II) at 183—184° (with decomposition), of *aa-diethylketopentamethylene* at 196—197°, and of *aa-diethylketohexamethylene* at 168—169°.

J. F. T.

Action of Sodium on Nitrobenzene. By Walther Löb (*Ber.*, 1897, **30**, 1572—1574).—The action of metallic sodium on chloronitrobenzene, bromonitrobenzene, and chloronitrotoluene in ethereal solution gives rise to compounds in which sodium has probably entered the nitro-group (von Hofmann and Geyger, *Ber.*, 1872, 5, 915); the compound from parachloronitrobenzene, a black, unstable substance, has the constitution $(C_6H_4Cl{\cdot}NNa)_2O$. It is now found that nitrobenzene gives rise to a similar compound, which probably has the formula $(NPhNa)_2O$, being the sodium derivative of phenylhydroxylamine anhydride.

Toluene (50 parts) is boiled with sodium (2—3 parts) in a reflux apparatus, and treated with small quantities of a solution of nitrobenzene (10 parts) in toluene (20 parts), the liquid being frequently agitated; a brownish-black substance separates, and, when perfectly dry, may be preserved without undergoing change. Water eliminates the metal from the compound, giving rise to caustic soda and an oil which has reducing properties, and quickly resinifies; benzoic chloride in ethereal solution acts on the substance in the cold, and methylic and ethylic iodides at higher temperatures.

M. O. F.

Combination of Metallic Salts with Organic Bases. By D. Tombeck (*Compt. rend.*, 1897, **124**, 961—963).—Aniline, like ammonia, precipitates solutions of the salts of several metals. With zinc chloride, it yields very small prismatic needles of the composition

$$ZnCl_2,2NH_2Ph,$$

corresponding with the compound formed by ammonia; with cadmium chloride, it forms an analogous compound, which separates in silky needles. Both compounds are only slightly soluble in water, are non-deliquescent, but turn brown when exposed to air, and begin to decompose when heated at 100°, with liberation of aniline.

Zinc and cadmium bromides form analogous compounds with very similar properties.

Zinc and cadmium iodides yield respectively the compounds

$$ZnI_2,NH_2Ph \text{ and } CdI_2,NH_2Ph.$$

The former crystallises in very long, slender needles, and the latter in bulky prisms. They are readily affected by oxygen, and are much more soluble in hot water than in cold.

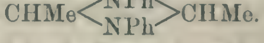
Halogen salts of other metals, and the higher homologues of aniline, as well as pyridines and amines of the paraffin series, form similar compounds.

C. H. B.

Action of Phosphorus Pentachloride on Aniline and its Salts. By J. Elliott Gilpin (*Amer. Chem. J.*, 1897, **19**, 352—363).—When phosphorus pentachloride (1 mol.) is heated with aniline hydrochloride (1 mol.) for 6—8 hours at 170° in a distilling flask, hydrogen chloride is evolved, and *trichlorophosphanil*, $PCl_3{:}NPh$, sublimes on to the cool part of the bulb. This substance decomposes into phosphoric and hydrochloric acids and aniline when it is boiled with water; with strong sulphuric acid, it yields sulphanilic acid. When aniline itself is treated with phosphorus pentachloride until no more action takes place, *chlorophosphotetranilide*, $PCl(NHPh)_4$, is formed; this substance is crystalline, and is very stable; it is unaffected by boiling with water, hydrochloric acid, or concentrated alkali, but heating with water at 180° hydrolyses it into phosphoric and hydrochloric acids and aniline. When it is heated, aniline, aniline hydrochloride, and some diphenylamine hydrochloride are given off; the black, amorphous residue contains carbon, nitrogen, and phosphorus, and is so stable that "only a small amount was decomposed when it was heated in a porcelain tube, in a current of oxygen, over the blast lamp for several hours." In consequence of the formation of this substance, the carbon in most of the compounds analysed could not be determined by combustion in the usual way; oxidation with dichromate and sulphuric acid had to be employed. When the tetranilide is treated with strong sulphuric acid, a compound, $OH\cdot P(NH\cdot C_6H_4\cdot SO_3H)_4$ is formed; this is very soluble in water, and so are its *barium* and *lead* salts, in both of which the metal appears to have replaced three-fourths of the hydrogen of the SO_3H groups.

Two additional compounds are formed when phosphorus pentachloride acts on aniline. The three toluidines also yield compounds analogous to chlorophosphotetranilide. C. F. B.

Some Reactions of Metadimethylamidophenol. By LÉON LEFÈVRE (*Bull. Soc. Chim.*, 1897, [iii], 15, 900—904).—A criticism of Rothenburg's description of the reaction of this substance (Abstr., 1895, i, 538). M. W. T.

Ethylidenediphenamine [Ethylidenedianiline]. By ALEXANDER EIBNER (*Ber.*, 1897, 30, 1444—1450).—Aniline readily reacts with acetaldehyde, either in aqueous solution or in the presence of alkali, to form *ethylidenedianiline*, $CHMe(NHPh)_2$, which is extremely unstable in the moist or impure state, but when pure crystallises in colourless, lozenge-shaped tablets which melt at 51°. It is completely decomposed by acetic anhydride, but reacts with a second molecule of acetaldehyde to form an amorphous, sparingly soluble substance which probably has the formula  $CHMe{<}{\begin{matrix}NPh\\NPh\end{matrix}}{>}CHMe$. Ethylidenedianiline is quantitatively converted by hydrocyanic acid into aniline, and the nitrile of ethylideneaniline (m. p. 92°). When it is allowed to remain in contact with water, or boiled with water or alcohol, it is converted into a mixture of the two stereoisomeric diethylidenedianilines.

It seems probable that the crystalline product described by Schiff (*Annalen*, Suppl., 3, 343) as ethylidenedianiline must have been one of its decomposition products, probably in an impure state. A. H.

Synthesis of Symmetrical Tetramidobenzene from Dinitrodichlorobenzene. By RUDOLF NIETZKI and A. SCHEDLER (*Ber.*, 1897, 30, 1666—1669).—The authors have prepared large quantities of Körner's 1 : 3-dichloro-4 : 6-dinitrobenzene (*Jahresber.*, 1875, 323) by the following method. One part of metadichlorobenzene is added to

12 parts of a mixture of fuming nitric acid (1 part) and concentrated sulphuric acid (2 parts), the mixture is kept well cooled and finally warmed for a short time on the water bath.

3 : 4 : 6-*Chlorodinitraniline*, which may be obtained by gently warming an alcoholic solution of this compound with alcoholic ammonia, crystallises in orange-yellow needles, melts at 174°, and when reduced with stannous chloride yields chlorotriamidobenzene. If, however, the dichlorodinitrobenzene is heated for 3 hours with alcoholic ammonia at 150°, both chlorine atoms become replaced by amido-groups, and Nietzki and Hagenbach's 4 : 6-dinitrometaphenylenediamine is formed (Abstr., 1887, 476). This compound, when reduced with stannous chloride, yields symmetrical tetramidobenzene. Chlorodinitrodiphenylamine $[(NO_2)_2:Cl:NHPh = 4:6:3:1]$, obtained by warming dichlorodinitrobenzene with an alcoholic solution of aniline, crystallises in orange-yellow needles and melts at 120°. *Dianilidodinitrobenzene* $[(NHPh)_2:(NO_2)_2 = 1:3:4:6]$ is obtained when dichlorodinitrobenzene is boiled with aniline; it crystallises in red prisms, melts at 186°, and when reduced yields *diphenyltetramidobenzene*,

$$C_6H_2(NH_2)_2(NHPh)_2\ [=1:3:4:6],$$

melting at 207°. The authors have so far not been able to obtain fluorindine from this compound by the aid of oxidising agents.

J. J. S.

Non-existence of Four Phenylparatolylmethenylamidines. By Henry L. Wheeler (*Amer. Chem. J.*, 1897, **19**, 367—374).—Contrary to Walther's statement (this vol., i, 242), only one phenylparatolylmethenylamidine exists. This melts at 103·5—104·5°, and is best made by the fourth method given by Walther, less well by the third. When the first method is employed, the product consists largely of diphenylmethenylamidine, which melts between 135° and 140°, whilst the product of the third method is largely diparatolylmethenylamidine, which melts at 140°.

C. F. B.

Hantzsch's Recent Work [Diazo-question]. By Christian W. Blomstrand (*Ber.*, 1897, **30**, 1265).—A short polemical notice on Hantzsch's communications (this vol., i, 240, 278).

J. J. S.

Migration of the Diazo-group. By Arthur R. Hantzsch and Frederick Mollwo Perkin (*Ber.*, 1897, **30**, 1412—1415).—The authors have observed that when parabromodiazoamidobenzene is prepared from diazonium chloride and parabromaniline, symmetrical dibromodiazoamidobenzene is one of the products; the action of diazonium chloride on parachlor- and paraiod-aniline proceeds in the same way, but the dihalogen compound does not arise from aniline and the substituted diazonium salt. These changes involve a partial exchange of the diazonium residue for the amido-group, a phenomenon observed for the first time by Griess (*Ber.*, 1882, **15**, 2190), and more recently by Schraube and Fritsch (Abstr., 1896, i, 221).

When an alcoholic solution of mercuric chloride is added to diazoamidobenzene dissolved in benzene, the *mercurochloride* of amidoazobenzene is produced; it separates from the mother liquor after filtration of the crystalline precipitate which is first formed, and crystallises in reddish-yellow, lustrous plates melting at 170°. The precipitate obtained in the first instance is separable by acetone into two constituents, the soluble substance consisting of diazonium mercurochloride, whilst the insoluble portion, which is free from chloride and yields phenol under the influence of hot dilute acids, is probably a mercury derivative. M. O. F.

Diazoic Acids [Alphylnitramines]. By EUGEN BAMBERGER (*Ber.*, 1897, 30, 1248—1263. Compare Abstr., 1893, i, 327, and 1894, i, 238).—In consequence of Pinnow's recent communication on nitramines (this vol., i, 338), the author is forced to publish the work which has already been accomplished by him and his pupils.

Benzenediazoic acid, $NHPh{\cdot}NO_2$, is readily diazotised, nitrous acid converts it almost quantitatively into diazobenzene nitrate; this property is also characteristic of alphylnitrosohydroxylamines (Abstr., 1895, i, 217) and is shared by nitramines generally.

Benzenediazoic acid O-methylic ether, and its paranitro-derivative are acted on by nitrous acid in a similar manner. The formation of phenylazonaphthol on the prolonged boiling of a benzene solution of benzenediazoic acid and β-naphthol is attributed by the author to the previous formation of nitrous acid.

Benzenediazoic acid is readily reduced by sodium amalgam to sodium isodiazotate, and a similar reduction may be brought about by the addition of zinc dust to a solution of potassium benzenediazoate and ammonium chloride.

Parachloro-, bromo-, and methyl-benzenediazoic acids have been reduced in a similar manner, and also nitrosoalphylhydroxylamines. O-methylic benzenediazoate (Abstr., 1894, i, 238) is hydrolysed to the acid when treated with methyl-alcoholic potash (25 per cent.) and water, potassium isodiazobenzene is also formed at the same time. The isomeric N-methylic salt, phenylmethylnitramine, under similar conditions, yields no trace of either of these products. Phenylmethylnitramine reacts with alkalis in very much the same way as secondary nitramines of the fatty series (Franchmont and Erp, Abstr., 1896, i, 298), the products being aniline, nitrous and formic acids. Paranitrophenylmethylnitramine, when treated in a similar manner, yields paranitraniline and also methylparanitraniline; the latter is probably formed by some secondary reaction.

[With ROBERT DIETRICH].—*Paranitrobenzenediazoic acid* crystallises in golden-yellow needles and melts at 110—111°; its *N-methylic ether*, $NO_2{\cdot}C_6H_4{\cdot}NMe{\cdot}NO_2$, melts at 140° and is volatile with steam, the *ethylic ether* melts at 90°. The *O-methylic ether*, $NO_2{\cdot}C_6H_4{\cdot}N_2O{\cdot}OMe$, melts at 109·5° and the *O-ethylic ether* at 83°.

[With CARL SEITZ].—*Metanitrorthotoluenediazoic acid* melts at 103°; its *sodium* salt crystallises in golden needles and its *silver* salt forms a yellow precipitate. Its *N-methylic* ether melts at 70·5° and its *O-methylic* ether at 110°.

[With ALFRED VOSS].—*Orthonitrobenzenediazoic acid* crystallises in pale yellow, glistening needles, or in brownish-yellow, strongly refractive plates; it melts at 65·5° and has an extremely sweet taste. Its *N-methylic* ether melts at 67°, and is slowly volatile with steam; acids decompose it, yielding 2 : 4- and 2- : 6-dinitromethylaniline. Its *O-methylic ether* is a brownish-yellow oil which is volatile with steam.

Metanitroparatoluenediazoic acid melts at 79° and is tasteless; its *N-methylic ether* melts at 105—105·5°, whereas the *O-ether* is a yellow oil.

[With ERNST HOFF].—*Paratoluenediazoic acid* crystallises in silver-white, glistening plates, or in glistening needles, and melts at 52—53°.

[With FRITZ STINGELIN].—*Orthotoluenediazoic acid* is a pale yellow oil, *both ethers* are also oils.

Parachlorobenezenediazoic acid melts at 81—82°, its *N-methylic ether* at 48—49°. The *silver, lead, potassium,* and *O-methyl* (oil) derivatives are also described.

Parachlororthonitrobenzenediazoic acid melts at 107—108°.

[With ARMAND STIEGELMANN].—*Parabromobenzenediazoic acid* melts at 102°, its *N-methylic ether* at 83·5—84·5°, whereas its *O-methylic ether* is an oil.

[With OTTOKAR BOECKING].—*β-Naphthalenediazoic acid*,

$$C_{10}H_7\cdot NH\cdot NO_2,$$

melts between 131·5° and 136°; its *N-methylic ether* melts at 109°, and its *O-methylic ether* at 40°.

All the above-mentioned diazoic acids were obtained either by the oxidation of *i*- or *n*-diazotates or by the action of acetic anhydride on alphylamine nitrates. In one case, parachloraniline nitrate, the product obtained by the aid of acetic anhydride was not parachlorobenzenediazoic acid but orthonitroparachlorobenzenediazoic acid. The N-ethers were prepared from the sodium salts and the O-ethers from the silver salts. In some cases, a mixture of the two ethers was obtained, not only from the silver salt, but also from the sodium salt.

The diazoic acids and also their N-ethers are readily transformed into nitrated amines having the nitro-group in the benzene nucleus by any of the following methods. 1. By boiling with dilute mineral acids. This is not a useful method in the case of extremely stable diazoic acids. 2. By passing hydrogen chloride into a cold ethereal solution of the acid. 3. By the action of a mixture of glacial acetic acid and concentrated sulphuric acid at 0—10°. If the last method is adopted, small quantities of diazonium salts are also formed. J. J. S.

Diazoamido-compounds. By ARTHUR R. HANTZSCH and FREDERICK MOLLWO PERKIN (*Ber.*, 1897, 30, 1394—1412).—From the fact that certain diazoamido-compounds of asymmetric structure frequently occur in two modifications, it has been conjectured that these must be represented by the tautomeric expressions $R^1\cdot N\colon N\cdot NHR^{11}$, and $R^1\cdot NH\cdot N\colon N\cdot R^{11}$; the authors describe numerous experiments for the purpose of throwing light on the properties, and conditions of production, of these isomerides.

The normal modification of parabromodiazoamidobenzene crystallises in flat, bright yellow needles, and melts at 104—105°, whether prepared from parabromodiazonium chloride and aniline, or from diazonium chloride and parabromaniline; without any apparent change in the conditions, one experiment in about four gives rise to the abnormal modification, which is produced more frequently from the first-named pair of substances. The abnormal modifications, for several are mentioned, sometimes form pale yellow crystals, but more usually separate in granular form, and melt variously at 65°, 79°, 85°, and 87°; the solutions in alcoholic potash are frequently deep red, the less readily fusible form yielding a yellow liquid. The authors discuss, and dismiss as improbable, explanations of these facts depending on stereoisomerism, the presence of a trace of the structurally isomeric bromamidoazobenzene, the existence of an equimolecular mixture of diazoamidobenzene and dibromodiazoamidobenzene, and the occurrence of a solid solution of this mixture in bromodiazoamidobenzene; it is also unlikely that an isomeride of the type $NH<\begin{matrix}N{\cdot}R\\ |\\ N{\cdot}R\end{matrix}$ is present. They prefer to regard the substance which melts definitely at 104—105° (the normal modification) as having the constitution $NPh{:}N{\cdot}NH{\cdot}C_6H_4Br$, the abnormal forms most probably consisting of the isomeride $NHPh{\cdot}N{:}N{\cdot}C_6H_4Br$, mixed with varying quantities of the less readily fusible compound. This view is confronted by two objections, namely, the incapacity of the less definite form to undergo transformation into the normal modification, and the identical chemical behaviour of the two forms. Boiling dilute sulphuric acid resolves both modifications into parabromaniline, aniline, phenol, and parabromophenol, whilst hydrogen chloride liberates from the solutions in petroleum a mixture of diazonium and bromodiazonium chlorides. Phenylcarbimide gives rise in both cases to the bromodiazocarbamide derivative described by Goldschmidt and Molinari (Abstr., 1888, 1283); this substance melts at 131° (compare *loc. cit.*), and yields bromodiphenylcarbamide when submitted to hydrolysis.

Normal parachlorodiazoamidobenzene, $NPh{:}N{\cdot}NH{\cdot}C_6H_4Cl$, crystallises in golden-yellow needles and melts at 87—88°; the abnormal modification, which occurs in the same erratic manner as the bromoderivative, usually melts at about 65°, and one preparation as low as 56—57°. The molecular refractions, determined for red light in 14·37 per cent. alcoholic solutions of the two forms, are 134·221 and 134·877 respectively. The action of phenylcarbimide on both modifications is identical.

Normal pariododiazoamidobenzene, $NPh{:}N{\cdot}NH{\cdot}C_6H_4I$, crystallises from petroleum in beautiful, golden-yellow needles, becoming greenish-brown under the influence of light, and melts at 118—119°; the abnormal modification is a brownish, sandy powder, which melts at 79—85°. *Paradi-iododiazoamidobenzene* melts at 165—166°.

Parachloroparabromodiazoamidobenzene, $C_6H_4Cl{\cdot}N{:}N{\cdot}NH{\cdot}C_6H_4Br$, is produced alike from chlorodiazonium chloride and bromaniline, and from bromodiazonium chloride and chloraniline, and crystallises in yellow needles melting at 138—139°; in the case of this substance, the occurrence of different modifications was not observed.

Diazoamidobenzenetoluene melts at 90—91°, and does not appear to give rise to abnormal modifications, and the same observation applies to nitrodiazoamido-compounds. M. O. F.

Formophenylhydrazide. By EUGEN BAMBERGER (*Ber.*, 1897, 30, 1263—1264).—Formophenylhydrazide, $NHPh{\cdot}NH{\cdot}COH$, was slowly heated until a vigorous evolution of gas occurred (about 220°); after being kept at a temperature of 190—210° for 2 hours, the mass was subjected to distillation with steam, and the residue recrystallised from alcohol. The product proved to be diphenyltetrazoline, and was in all respects identical with the compound described by Ruhemann (Trans., 1888, **53**, 850). (Compare also Pellizari, this vol., i, 231). J. J. S.

Phenylhydrazones from Aldehydes. By EMIL FISCHER (*Ber.*, 1897, **30**, 1240—1243).—The author has repeated his work on the action of phenylhydrazine on acetaldehyde, benzaldehyde, and salicylaldehyde (Abstr., 1896, i, 361) in consequence of work recently published by Causse (Abstr., 1896, i, 611). All the results previously published are confirmed, and the author concludes that all Causse's analytical results and also the speculations based thereon are absolutely false. J. J. S.

Molecular Rearrangement of the Oximes by Means of Certain Metallic Salts. By WILLIAM J. COMSTOCK (*Amer. Chem. J.*, 1897, **19**, 485—492).—Besides the ordinary reagents, the author finds that several metallic salts, notably cuprous chloride and bromide and antimony trichloride, are capable of producing the Beckmann rearrangement of an oxime into amide or substituted amide. A molecular compound of the aldoxime or ketoxime with the cuprous salt is first formed, but the change of this cuprous-haloid-oxime into an amide is not a general reaction, as in some cases the greater part of the oxime is decomposed with regeneration of aldehyde or ketone.

The tendency of benzaldoxime and acetoxime to form molecular compounds with cuprous chloride is so great that they reduce cupric chloride to cuprous chloride. A portion of the oxime is split up into the aldehyde or ketone and hydroxylamine, which latter reduces the cupric chloride to cuprous chloride with formation of nitrous acid, whilst another portion of the oxime unites with the cuprous chloride thus formed with the production of the difficultly soluble cuprous-chloride-oxime.

Cuprous chloride benzsynaldoxime, $(CHPh\colon NOH)_2,CuCl$, is formed when a cold solution of ordinary benzaldoxime in dry toluene is treated with a slight excess of cuprous chloride, and the filtered solution precipitated with light petroleum, or by mixing benzaldoxime dissolved in alcohol with an alcoholic solution of cupric chloride. It forms colourless needles, which become dark green very quickly on exposure to air, and show no sharp melting point. The copper can be removed by dilute sodium hydroxide solution, and on passing carbonic acid gas through the filtered solution benzsynaldoxime separates out.

The rearrangement of benzaldoxime into benzamide was carried out in benzene or toluene solution, the amide being obtained with sharp melting point after one crystallisation.

Cuprous bromide acts in a similar way to the chloride, but the intermediate product appears to be more stable.

Cinnamaldoxime, gives with cuprous bromide an additive product, crystallising from toluene in small, yellow needles. On boiling the toluene solution, rearrangement takes place, with production of the amide of cinnamic acid.

Œnanthaldoxime forms, with cuprous bromide in light petroleum solution, a product crystallising in beautiful, star-like clusters of long, transparent prisms.

Cuprous chloride acetoxime, $(C_3H_6{:}NOH)_2,CuCl$, crystallises from boiling light petroleum in colourless, transparent plates or inclined prisms, which become yellow on exposure to the air, and have no definite melting point. The corresponding *cuprous bromide* compound crystallises in hexagonal plates or thick, transparent, inclined prisms melting at 121—122°. Rearrangement into methylacetamide could not be effected by boiling the toluene solution of either of these acetoxime derivatives.

Acetophenoneoxime unites with cuprous chloride in toluene solution, forming a compound which crystallises from light petroleum in thin, colourless plates which rapidly darken.

Benzophenoneoxime gives, with cuprous chloride, a compound crystallising in diamond-shaped, doubly-terminated plates of yellow colour. On boiling a toluene solution of the oxime and cuprous chloride or bromide, benzophenone is produced; but if the oxime is gradually added to antimony trichloride warmed just above its melting point, benzanilide is obtained. A. W. C.

Action of Ethylic Chloroformate on Formanilide. By HENRY L. WHEELER and H. F. METCALF (*Amer. Chem. J.*, 1897, **19**, 217—227).—The oil obtained, in addition to diphenylformamidine hydrochloride, when formanilide is treated with ethylic chloroformate, is not ethylisoformanilide, as Freer and Sherman think (Abstr., 1896, i, 611). It does not contain a trace of this substance, but consists of formylphenylurethane, together with a little phenylurethane. The gas evolved in the reaction consists of carbonic anhydride, carbonic oxide, and ethylic chloride. *Formylphenylurethane*, $CHO\cdot NPh\cdot COOEt$, may be obtained pure by treating ethylisoformanilide, $OEt\cdot CH{:}NPh$, with a slight excess of ethylic chloroformate; it boils at 149—151° under 15 mm. pressure, gives α-formophenylhydrazide when treated with phenylhydrazine, and is readily hydrolysed to phenylurethane when boiled with alkali.

Arguments are brought forward in favour of the formula

$$OH\cdot CH{:}NPh$$

for formanilide, and Claisen's reasoning (Abstr., 1896, i, 91) on behalf of the formula $H\cdot CO\cdot NHPh$ is shown to be open to objection.

C. F. B.

Some Anilides of Phthalic Acid. By M. ROGOFF (*Ber.*, 1897, **30**, 1442—1443).—*Phthalanilide* melts and decomposes at 231°. When boiled with acetic acid, it yields phthalanil. *Phthalo-ψ-cumidide*, $C_6H_4(CO\cdot NH\cdot C_6H_2Me_3)_2$, melts at 227°, and crystallises in needles. *Dimethylphthalanilide*, $C_6H_4(CO\cdot NPhMe)_2$, crystallises in needles and melts at 177—177·5°. A. H.

Urethanes. By OTTO FOLIN (*Amer. Chem. J.*, 1897, **19**, 323—352).—Bromamides, when boiled with sodium methoxide in methyl-alcoholic solution, react and yield urethanes (alkyl carbamates) in accordance with the equation $R\cdot CO\cdot NHBr + NaOMe = NaBr + R\cdot NH\cdot COOMe$, a molecular transformation taking place not unlike the Beckmann transformation, and that involved in the Hofmann method of preparing aliphatic amines. The bromamides were prepared by adding the amides to a solution of bromine in aqueous potassium hydroxide; they all appear to react in the manner described, alike when R is a positive radicle (Ph, $C_6H_4\cdot NO_2$, C_6H_4Br), and a more negative one ($CH_2\cdot CH_2\cdot NH\cdot COOEt$); indeed, the reaction seems well adapted for the preparation of urethanes. The new compounds obtained, with their melting points, are as follows: *Methylic metanitrophenylcarbamate*, yellow, 147—149°; *methylic orthonitrophenylcarbamate*, greenish-yellow, 53° (if the reaction is carried out at 30°, orthonitrobenzoylorthonitrophenylcarbamide, $NO_2\cdot C_6H_4\cdot NH\cdot CO\cdot NH\cdot CO\cdot C_6H_4\cdot NO_2$, is also formed; compare Swartz, this vol., i, 410); *metabromobenzobromamide*, 105°, *methylic metabromophenylcarbamate*, 84·5—85·5°; *carbomethoxy-β-amidopropionobromamide*, 117—118°. Incidentally, there were prepared *paradiethylamidobenzoic chloride*, by the action of phosphorus pentachloride on the hydrochloride of the acid (not on the acid itself, which has possibly a betaine constitution), and from this the *amide* melting at 136—137°; the ethylic salt of the acid was found to melt at 43°, whereas it has been described previously as liquid at ordinary temperatures; further, paradimethylamidobenzonitrile, also described as an oil, was found to melt at 74—76°, and it was found that, by the action of cyanogen bromide on dimethylaniline, and on parabromodimethylaniline in the presence of sodium, the product obtained in both cases was the last-named substance, no cyanide being formed.

The action of phosphorus pentachloride on urethanes was studied, usually by mixing the two substances, adding chloroform, and passing a current of hydrogen chloride through the mixture until all the phosphorus oxychloride had been carried off. The normal product of the reaction is a substituted amide of chloroformic acid, $R\cdot NH\cdot COOEt + PCl_5 = POCl_3 + EtCl + R\cdot NH\cdot COCl$, and the reaction affords a convenient method for preparing both such chloroformamides and the carbimides into which they are converted when they are heated in a current of hydrogen chloride. Chloroformometanitranilide, melting at 102°, was prepared in this way; it yields metanitrophenylcarbamide when treated with ammonia, and, when heated at 110—140° in a current of hydrogen chloride yields *metanitrophenylcarbimide;* this melts at 49—50°, is devoid of odour, and yields methylic metanitrophenylcarbamate with absolute methylic acohol, and *metanitrobenzoylmetanitrophenylcarbamide*, melting at 230°, when heated at 150° with metanitrobenz amide. Chloroformometabromanilide was also prepared; with ammonia it yields *metabromophenylcarbamide*, which softens at 162°, and melts at 164—165°. On urethane itself (ethylic carbamate), the action of phosphorus pentachloride is more complicated; instead of $NH_2\cdot COCl$, such derivatives as $PCl_2\cdot NH\cdot COCl$ or $POCl_2\cdot NH\cdot COCl$ appear to be formed. Urethane was conveniently prepared by adding a saturated solution of potassium isocyanate in 50 per cent. alcohol to an excess of strong alcoholic hydrochloric acid, and allowing the mixture to remain for 24 hours at the ordinary temperature.

The action of carbonyl chloride (phosgene) on urethane itself was studied by heating the two substances together for half an hour in a sealed tube at 75°. Three products were obtained: (1) *Chloroformyl-*

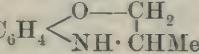
urethane, COOEt·NH·COCl, as was shown by the fact that the product of the reaction, when treated with aniline, gave ethylic phenylallophanate, COOEt·NH·CO·NHPh, melting at 106°, and identical with the substance prepared from urethane and chloroformanilide (the melting point, 120°, hitherto accepted is erroneous). (2) *Carbonyldiurethane*, $CO(NH·COOEt)_2$, which melts at 107°, yields a *mono-silver* derivative, and is a very stable substance, for it can be heated in a sealed tube for half an hour at 75—80° with a benzene solution of hydrogen chloride without undergoing any change. A better yield of this substance was obtained by heating one mol. of carbonyl chloride with two mols. of urethane and some pyridine for half an hour in a sealed tube at 85°. (3). A small quantity of ethylic allophanate $COOEt·NH·CO·NH_2$. C. F. B.

Orthocyanobenzaldehyde. By Theodor Posner (*Ber.*, 1897, 30, 1693—1700).—Although meta- and paracyanobenzaldehydes may be prepared by the action of copper nitrate on the corresponding cyanobenzylic chlorides, the ortho-compound cannot be obtained in this way; the oxime, however, is obtained from orthocyanobenzylic chloride under the influence of alcoholic hydroxylamine.

Orthocyanobenzaldoxime, $CN·C_6H_4·CH{:}NOH$, crystallises from ethylic acetate and melts at 173°, resolidifying at this temperature, and subsequently fusing at 203°; it is insoluble in water, and dissolves slowly in caustic potash, yielding ammonia and phthalimide. The *hydrochloride* melts at 182°. When carefully heated with acetic anhydride, the oxime may be crystallised from this agent; but if the substances are heated together in a reflux apparatus, orthophthalonitrile is produced; this substance, when purified, is odourless (compare Pinnow and Sämann, Abstr., 1896, i, 367).

Orthocyanobenzaldoxime has the *syn*-configuration, and fusion does not convert it into the isomeric form. The phenomenon observed on melting the substance is due to the production of *orthophthalonitrilamide* (*orthocyanobenzamide*), $CN·C_6H_4·CO·NH_2$, which separates from ethylic acetate in colourless crystals and melts at 203°; alkalis convert it into phthalimide. M. O. F.

Nitrophenacetols [Nitrophenoxyacetones] and a Synthesis of 2′-Methylphenomorpholine (2′-Methyldihydrophenoparoxazine). By Richard Stoermer and H. Brockerof (*Ber.*, 1897, 30, 1631—1641. Compare Abstr., 1887, 464).—*Paranitrophenoxyacetone*, $NO_2·C_6H_4·O·CH_2·COMe$, is best prepared by heating finely-divided potassium paranitrophenoxide (1 mol.) with chloracetone (6 mols.) for about 3 hours at a temperature just below the boiling point of the latter. The excess of the chloracetone is removed by distillation with steam, and the residue is crystallised several times from water and from alcohol. It crystallises in yellowish plates, and melts at 81°; it is readily soluble in ether or chloroform, and also in boiling water, but is less soluble in cold water or alcohol. Alkalis dissolve the compound, yielding deep yellow solutions, from which it can be recovered on acidifying. The *semicarbazone*, $NO_2·C_6H_4·O·CH_2·CMe{:}N·NH·CO·NH_2$, is sparingly soluble in water, alcohol, or ether, and melts and decomposes at 216°. The *phenylhydrazone* melting at 140°, the *oxime* melting at

119°, and the *sodium hydrogen sulphite* derivative are all described. *Orthonitrophenoxyacetone* may be obtained in a somewhat similar manner by the action of chloracetone on dry powdered potassium orthonitrophenoxide made into a cream with acetone. The mixture is first heated to 90°, and when the reaction is complete, is further heated at 115—120° for $1\frac{1}{2}$ hour. After distillation with steam, the residue is recrystallised from alcohol, and then from water. The nitrophenoxyacetone crystallises in colourless, long, silky needles, melts at 69°, and is readily soluble in the usual organic solvents. The *semicarbazone*, melting at 178°, the *phenylhydrazone*, melting at 101°, the *oxime*, melting at 102°, and the sodium hydrogen sulphite compound are all described. When reduced with tin and hydrochloric acid, orthonitrophenoxyacetone yields two bases, which may be separated by steam distillation; a considerable quantity of an oily secondary base passes over first, and then a small quantity of a tertiary crystalline base. The oily base, *2′-methylphenomorpholine*,  $C_6H_4<\begin{matrix}O—CH_2\\ \vert \\ NH\cdot CHMe\end{matrix}$ (*2′-methyldihydrophenoparoxazine*) distils at 150—152° under a pressure of 24 mm. Its sp. gr. = 1·1148 at 15°, and its refractive index $n_{(D)} = 1·577$. When freshly distilled, the oil is quite colourless, but gradually turns yellow. The *hydrochloride*, $C_9H_{11}NO,HCl$, forms rhombic crystals readily soluble in alcohol or water. The *platinochloride*, $(C_9H_{11}NO)_2,H_2PtCl_6$, forms a yellowish-brown, crystalline precipitate, melts at 197°, and cannot be recrystallised from water or alcohol. The *carbamide*, $NH_2\cdot CO\cdot C_9NH_{10}O$, melting at 119°; *thiocarbamide* melting at 93°; *phenylcarbamide*, $NHPh\cdot CO\cdot C_9NH_{10}O$, melting at 138°; *phenylthiocarbamide* melting at 125°; *acetyl* derivative, $C_9H_{10}NOAc$, melting at 87°; *benzoyl* derivative melting at 126°; the *picrate*,

$$C_9H_{11}NO,C_6H_2(NO_2)_3OH,$$

melting at 141°, and *nitrosamine*, $C_9H_{10}NO\cdot NO$, are all described. The latter is a thick, dark-yellow oil with an odour of peppermint, and decomposes on heating; it yields a *nitronitrosamine*, $C_9H_9NO\cdot(NO)(NO_2)$, crystallising in orange-yellow, glistening crystals. This nitro-compound is sparingly soluble in cold alcohol or water, melts at 159°, and on boiling with concentrated hydrochloric acid yields *nitromethylphenomorpholine*, $C_9H_{10}NO\cdot NO_2$, melting at 132°. This nitro-compound, when reduced with tin and hydrochloric acid, yields *amidomethylphenomorpholine*, which is a brownish, strongly basic oil reacting with phenyl cyanate to form a compound melting at 207°.

The crystalline tertiary base, $C_9H_{13}NO_3$ or $C_9H_{12}NO_3$, formed at the same time as the methylphenomorpholine, melts at 106°, crystallises in colourless plates, and is extremely stable.

By reducing an alcoholic solution of orthonitrophenoxyacetone with stannous chloride at the ordinary temperature, the authors have succeeded in obtaining a small quantity of an unstable base, *a-methylphenoparoxazine*, which yields a platinochloride melting above 250°.

J. J. S.

A General Reaction of Aromatic Ketones. By SIEGFRIED BLUMENFELD and PAUL FRIEDLÄNDER (*Ber.*, 1897, 30, 1464—1465).—When a quinone is heated with a phenol and a little dilute sulphuric acid, a colourless product is formed which is isomeric with the corresponding quinhydrone. The product from *a*-naphthaquinone and pyrogallol melts with decomposition at 240—246° (uncorr.) and is insoluble in water. A. H.

Supposed Decompositions in the Mesitylene Series. By VICTOR MEYER and WILHELM MOLZ (*Ber.*, 1897, **30**, 1270—1277. Compare Abstr., 1896, i, 418, 419, and this vol., i, 142, 181).—The authors have been able to prove that acetomesitylene obtained by the Friedel-Craft method from pure mesitylene is absolutely pure, and contains no isomeric compound as suggested by Lucas. This has been established by the fact that the ketone on further acetylation with a large excess of aluminium chloride is completely converted into the diacetyl derivative of mesitylene. It therefore follows that no intramolecular decomposition takes place during the acetylation of mesitylene. On oxidation, acetomesitylene yields varying quantities of mesitylglyoxylic acid and symmetrical trimethylmandelic acid,

$$C_6H_2Me_3\cdot CH(OH)\cdot COOH.$$

The glyoxylic acid when subjected to dry distillation, yields practically pure mesitylcarboxylic acid; the mandelic acid when subjected to the same treatment loses oxygen and yields mesitylacetic acid,

$$C_6H_2Me_3\cdot CH_2\cdot COOH.$$

Other reactions occur at the same time, and considerable quantities of carbon and water are formed. The acid which Lucas (this vol., i, 181) regarded as prehnitic acid is therefore mesitylacetic acid, the melting points of the two acids are practically identical, but analyses of the acid obtained by distilling the mandelic acid, and also analyses of the silver salt, proved the acid to be mesitylacetic acid. J. J. S.

Gallacetophenone. By R. LÖWY (*Ber.*, 1897, **30**, 1465—1466).—*Triacetylgallacetophenone* is formed when gallacetophenone is boiled for a very short time with acetic anhydride and sodium acetate. It forms colourless, thick crystals, melts at 83° and is not coloured in alcoholic solution by ferric chloride. It is converted by bromine into *triacetylgallacetophenone bromide*, which melts at 103° and yields the same condensation products with aldehyes as the chloride. A. H.

Mesitylenediketones. By HERMANN WEIL (*Ber.*, 1897, **30**, 1285—1286).—Pavia and V. Meyer have shown that in 1:3:5-substituted hydrocarbons of the benzene series, two acetyl groups can be introduced by treatment with acetic chloride in the presence of excess of aluminium chloride, and the author has now prepared other diketones of this class, using various acid chlorides for the purpose.

Dipropionylmesitylene, $C_6HMe_3(COEt)_2$, crystallises from light petroleum in colourless aggregates melting at 101—102°, and boiling without decomposition at 327° (uncorr.).

Dibutyrylmesitylene, $C_6HMe_3(COPr^a)_2$, separates from ether in colourless crystals melting at 36°, and boiling with slight decomposition at 338—339° (uncorr.).

Di-isobutyrylmesitylene, $C_6HMe_3(COPr^\beta)_2$, boils at 331—332° (uncorr.), and was not obtained in a crystalline condition.

Divalerylmesitylene, $C_6HMe_3(CO\cdot C_4H_9)_2$, boils at 210—211°, and slowly solidifies to colourless crystals melting at 55°.

Diœnanthylmesitylene, $C_6HMe_3(CO\cdot C_6H_{13})_2$, is a yellow oil distilling at 255° (18—20 mm.).

Attempts to form mixed compounds of this class were unsuccessful. On treating monacetylmesitylene with propionic chloride, dipropionylmesitylene is alone produced, and similarly on treating monopropionylmesitylene with acetic chloride, diacetylmesitylene is the sole product.

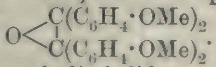
J. F. T.

Aromatic Thioketones and Resorcinol Dimethyl Ether [1:3-Dimethoxybenzene]. By GEORG HOSTMANN (*Chem. Centr.*, 1896, ii, 663—664; from *Diss. Rostock*, 1895, 1—40).—By condensation with thiophosphoryl chloride in presence of aluminium chloride, orthochloranisoil, which boils at 198—199° and is obtained from the diazo-compound of orthanisidine by means of cuprous chloride, forms lustrous, green needles of the *thioketone*,

$$CS(C_6H_3Cl\cdot OMe)_2\ [CS:Cl:OMe = 1:3:4],$$

which melts at 178—179°, and forms a blue solution in boiling alcohol. The sulphur may be removed by means of alcoholic potassium hydroxide solution and the corresponding oxygen *ketone* obtained in white needles melting at 183—184°. By heating with powdered copper obtained by reduction, the thioketone is converted into the tetraphenylethylene derivative, $C(C_6H_3Cl\cdot OMe)_2{:}C(C_6H_3Cl\cdot OMe)_2$, which melts at 257°.

The following compounds are prepared similarly to the above. The thioketone of orthochlorphenetoil forms dark-green needles, and melts at 141—142°; the corresponding ketone, white needles, melts at 122—123°, and the tetraphenylethylene derivative melts at 258—259°. Orthobromanisoil boils at 208—209°, the *thioketone* forms dark-green needles, melts at 189—190°, and gives a blue solution in boiling alcohol—in this preparation an excess of water should be avoided; the corresponding *ketone* melts at 180—181°. The thioketone prepared by Rosenberg from phenylic propylic ether melts at 108—109°, and, on heating with copper, is converted into the corresponding tetraphenylethylene derivative, which forms fine needles and melts at 139—140°. The corresponding *ketone* crystallises in broad leaflets. By means of the same reaction, the thio-derivative of Michler's ketone yields lustrous crystals of the ethylene derivative, which melts at 310—315°. By reduction with sodium and alcohol, the ethylene derivative of phenetoil, which melts at 121—122°, is partially converted into the corresponding ethane derivative which, on crystallisation from glacial acetic acid, forms needles; it is insoluble in boiling alcohol, and melts at 163—164°. The ethylene derivatives of this series, containing no halogen, undergo a reaction with lead dioxide with production of a fugitive blue colour, but those containing halogens do not give this reaction. This blue compound has not been prepared in a pure state, but an intermediate product obtained by the action of lead dioxide (1 mol.) on the tetraphenylethylene derivative from anisoil (2 mols.), after crystallisation from boiling glacial acetic acid, forms colourless, transparent crystals, melts at 188—189°, and corresponds in composition to tetraphenylethylene oxide,



$$O<\begin{matrix}C(C_6H_4\cdot OMe)_2\\ |\\ C(C_6H_4\cdot OMe)_2\end{matrix}.$$

By the action of potassium methoxide and methylic iodide on resorcinol, the dimethyl ether, which melts at 214—220°, is the main product, but by using sodium ethoxide and a large excess of methylic iodide and heating at 170—180° for 8 hours, products of higher boiling point are obtained. By submitting the fraction boiling at 240—250° to Gattermann and Hartmann's method of hydrolysis by means of aluminium chloride at 120°, methylic chloride and trimethylresorcinol are formed, hence this fraction contains the dimethyl ether of trimethylresorcinol (mesorcinol),

$$C_6HMe_3(OMe)_2\ [Me_3 : (OMe)_2 = 1:3:5:2:4].$$

By the action of bromine, resorcinol dimethyl ether yields a dibromide which melts at 141°, and by the action of succinic anhydride in presence of aluminium chloride, dimethoxybenzoylpropionic acid,

$$C_6H_3(OMe)_2\cdot CO\cdot CH_2\cdot CH_2\cdot COOH,$$

which melts at 147°, and forms an oxime which melts at 161°. Both the acid and its oxime, when heated, form blue compounds which are probably closed chain condensation products. E. W. W.

Preparation of Metabromobenzoic Acid and Metabromonitrobenzene. By HENRY L. WHEELER and B. W. McFARLAND (*Amer. Chem. J.*, 1897, 19, 363—367).—Sealed tubes are not necessary in the preparation of metanitrobenzoic acid; benzoic acid (20 grams) may be heated with iron wire or gauze (6 grams) to 170° in a reflux apparatus, and in the course of 1½ hour, 48 grams of bromine (that is, a few grams more than are necessary to form the monobromo-derivative together with ferrous bromide) allowed to drop in, the temperature rising meanwhile to 260°; the yield of the pure product is nearly equal to the weight of the benzoic acid taken. If a similar experiment is carried out in a sealed tube at 225°, a much larger proportion of bromine being employed, the product is perbromobenzene, C_6Br_6.

Metabromonitrobenzene can be prepared in a similar fashion; the yield varies from 65—85 per cent. of the theoretical. Paradichlorobenzene yields a dibromo-derivative melting at 148°, presumably 1 : 4-dichloro-2 : 5-dibromobenzene. C. F. B.

Preparation of 2:4:6-Tribromobenzoic Acid from 2:4:6-Tribromaniline. By RUDOLF WEGSCHEIDER (*Monatsh.*, 1897, 18, 217—222).—In repeating Sudborough's experiments (Abstr., 1894, i, 244), it was found that the residue insoluble in alkali, obtained in the hydrolysis of the crude nitrile, is not unchanged nitrile but consists of resin 50, 1 : 2 : 4 : 6-chlorotribromobenzene 30, and 1 : 3 : 5-trichlorobenzene 20 per cent. The last substance was probably formed by exchange of bromine for chlorine during the heating with hydrochloric acid; the second presumably in the Sandmeyer reaction, hydrochloric acid being present in the diazo-solution.

The following melting points were found: 2 : 4 : 6-tribromaniline, 120—121°; 2 : 4 : 6-tribromobenzoic acid, 188—189°; 1 : 2 : 4 : 6-chlorotribromaniline, 87—88°. C. F. B.

***c*-Durenecarboxylic Acid.** By VICTOR MEYER and WILHELM MOLZ (*Ber.*, 1897, 30, 1277—1280).—Of the three durenecarboxylic acids, two, namely, those from durene and isodurene, have already been prepared and investigated, and the present paper deals with the preparation and properties of the third, that is, consecutive durenecarboxylic acid. This acid is not so readily prepared as its isomerides, the best method being by the carboxylation of consecutive durene (prehnitene). This hydrocarbon (which must be quite pure, when it boils at 202—204°) on treatment with urea hydrochloride and aluminium chloride is converted into the *amide*, a substance crystallising from alcohol in glistening needles melting at 222°. On hydrolysis by means of sodium nitrite, it yields consecutive *durenecarboxylic acid* (1 : 2 : 3 : 4-tetramethylbenzenecarboxylic acid), which crystallises from light petroleum in slender, white needles melting at 168—169°; when etherified by Emil Fischer's method, it yields 97 per cent. of ethylic salt, and can by this means be readily separated from its isomerides, which, under similar conditions, are not etherified. J. F. T.

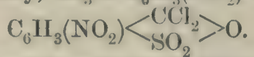
Derivatives of Parahydroxybenzoic Acid and of Anisic Acid. By KARL AUWERS (*Ber.*, 1897, **30**, 1473—1478).—The earlier descriptions of 3-chloro-4-hydroxybenzoic acid (Peltzer, *Annalen*, 1868, **146**, 286; Lössner, *J. pr. Chem.*, 1876, [ii], **13**, 432; Hasse, Abstr., 1878, 416) being so contradictory, the author has prepared it from 3-amido-4-hydroxybenzoic acid (this vol., i, 341). The acid has most of the properties given by previous authors, but melts at 165—166°; its *methylic* salt crystallises in flat needles and melts at 106—107°.

3-Iodo-4-hydroxybenzoic acid, prepared in a similar manner, crystallises in flat, glistening needles and melts at 173·5—174·5°. The author has also obtained the acid by Peltzer's method (*loc. cit.*), and finds that it then also melts at 173·5—174·5° instead of 160° as previously given. Its *methylic* salt crystallises in glistening needles and melts at 155—156°.

By reducing methylic metanitroanisate (Goldschmidt and Polonowska, Abstr., 1887, 1041) with aluminium amalgam and dilute alcohol, the author has obtained methylic metamidoanisate melting at 85—86°, and, on hydrolysis, the free acid melting at 204°, this acid being identical with the one obtained by Balbiano (*Gazzetta*, **14**, 247). The same acid is also obtained by reducing the nitro-acid with alcoholic ammonium sulphide or with tin and hydrochloric acid; in the former case, the yield is extremely poor, and the acid usually has a lower melting point (198°) owing to the presence of impurities. This accounts for the low melting points previously given by Zinin (*Annalen*, **92**, 327) and by Paternò and Oliveri (*Gazzetta*, **12**, 93). *Methylic metachloranisate*, obtained from the above methylic amidoanisate by Sandmeyer's reaction, melts at 94·5—95·5, and on hydrolysis yields the free acid melting at 213°. (Compare Schall and Dralle, *Ber.*, 1884, **17**, 2529.) J. J. S.

Some Salts of the Phthalic Acids, and the Author's Crystal-water Theory. By THEODORE SALZER (*Ber.*, 1897, **30**, 1496—1498). —The author describes various salts of phthalic, isophthalic, and terephthalic acids, and remarks that in most instances the water of crystallisation contained in them is in accordance with that demanded by his crystal-water theory. J. F. T.

Isomeric Chlorides of Paranitrorthosulphobenzoic Acid. By IRA REMSEN and G. W. GRAY (*Amer. Chem. J.*, 1897, **19**, 496—511. Compare Abstr., 1895, i, 472, 473, 474; this vol., i, 243, 244).—The authors have succeeded in preparing both the acid chlorides of nitrosulphobenzoic acid, namely, $SO_3Cl\cdot C_6H_3(NO_2)\cdot COCl$ and



$$C_6H_3(NO_2){<}\begin{matrix}CCl_2\\SO_2\end{matrix}{>}O.$$

Paranitrorthosulphobenzoic acid is obtained by treating paranitrotoluene with fuming sulphuric acid, and oxidising the paranitrorthotoluenesulphonic acid so produced with potassium permanganate. When the potassium salt of the acid is heated at 150° with phosphorus pentachloride, both the above mentioned chlorides are produced, and are separated by their different solubilities in chloroform, or by treating the chloroform solution of the chlorides with dilute ammonia. An 80—90 per cent. yield of the *unsymmetrical chloride* is obtained which crystallises from light petroleum in fine, white needles or long, flat plates melting at 56—57° (uncorr.), and decomposing when heated above 160°. The yield of *symmetrical chloride* is from 10—20 per cent., and it forms crystals showing monoclinic pinacoids and basal plane, and melts at 94—95° (uncorr.). It can be heated in sealed tubes to 150° with phosphorus oxychloride without undergoing decomposition. Cold water acts slowly on both chlorides, but, on boiling, decomposition is complete in a few minutes, being equally rapid in both cases. Dilute potash produces potassium hydrogen paranitrorthosulphobenzoate from both chlorides.

The symmetrical chloride, on treatment with dilute ammonia, gives the ammonium salt of paranitrobenzoicsulphinide, which crystallises in rectangular plates of glistening flakes, and does not melt below the boiling point of sulphuric acid.

Paranitrobenzoicsulphinide is produced as fine needles or plates, melting at 209° (uncorr.) on adding hydrochloric acid to the above-mentioned acid potassium salt. The *methylic* and *ethylic* salts are produced on heating the sulphinide in sealed tubes with the corresponding alkylic iodide; the former crystallises in leaf-like crystals melting at 179° (uncorr.), and the latter in needles melting at 172° (uncorr.).

Paranitrocyanobenzenesulphonic Acid, $NO_2\cdot C_6H_3(CN)\cdot SO_3H$.—The unsymmetrical chloride gives the ammonium salt of this acid when treated with dilute ammonia. The free acid is formed when its silver salt is treated with hydrochloric acid or its barium salt with sulphuric acid. It crystallises in long prisms, and melts between 145—150°. On heating with caustic potash, ammonia is liberated, and then, on adding hydrochloric acid, the acid potassium paranitrorthosulphobenzoate is obtained.

Paranitrocyanobenzenesulphonic chloride, $NO_2\cdot C_6H_3(CN)\cdot SO_2Cl$, is formed when the potassium salt of the acid is treated with phosphorus pentachloride; it crystallises in long, rectangular prisms, which melt at 107—108° (uncorr.).

Paranitrocyanobenzenesulphonamide, $NO_2\cdot C_6H_3(CN)\cdot SO_2\cdot NH_2$, is formed when the acid chloride is treated with ammonia. It crystallises in small, rectangular blocks resembling cane-sugar, and does not melt below 270°.

Paranitrocyanobenzenesulphonanilide, $NO_2\cdot C_6H_3(CN)SO_2\cdot NHPh$, crystallises in fine needles, and melts at 207—208° (uncorr.).

The *silver*, *potassium*, *barium*, *calcium*, *magnesium*, and *zinc* salts of paranitrocyanobenzenesulphonic acid and paranitrobenzoicsulphinide are also described. A. W. C.

Derivatives of Orthobenzoicsulphinide ("Saccharin"). II. By Hugo Eckenroth and Georg Koerppen (*Ber.*, 1897, 30, 1265—1269. Compare Abstr., 1896, i, 304 and 438).—A better yield of ethylenediorthobenzoicsulphinide (*loc. cit.*) is obtained when benzoicsulphinide, ethylenic bromide, and alcohol are heated for several days in a flask, using a reflux condenser. The product is washed with alcohol to remove the bromethyl compound, and is then crystallised several times from acetic acid. The ethylene compound forms thick, glistening crystals, and melts at 245—246°.

Hydroxyethylorthobenzoicsulphinide, $C_6H_4{<}\genfrac{}{}{0pt}{}{CO}{SO_2}{>}N\cdot C_2H_4\cdot OH$, is obtained when dilute caustic soda is carefully added to a solution of bromethylorthobenzoicsulphinide in hot water, and after some hours' heating the product acidified. It crystallises in needles, melts at 183°, and is readily soluble in alcohol, benzene, and acetic acid.

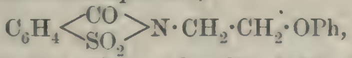
A small quantity of *methylenediorthobenzoicsulphinide* may be obtained by the action of formaldehyde and sulphuric acid on benzoicsulphinide. It crystallises in six-sided plates and melts at 290°.

Ethylic orthobenzoicsulphinidecarboxylate, $C_6H_4{<}\genfrac{}{}{0pt}{}{CO}{SO_2}{>}N\cdot COOEt$, is a crystalline powder which melts at 136° and is readily soluble in alcohol or ether. When boiled for some time with water, it is decomposed into benzoicsulphinide, alcohol, and carbonic anhydride.

Methylic orthobenzoicsulphinideacetate, $C_6H_4{<}\genfrac{}{}{0pt}{}{CO}{SO_2}{>}N\cdot CH_2\cdot COOMe$, melts at 118° and the *ethylic* salt at 104°. Both are readily soluble in the usual organic solvents.

Benzoylorthobenzoicsulphinide, obtained by the action of benzoic chloride on benzoicsulphinide at 225° for 2 hours, crystallises in colourless needles, melts at 165°, and is readily soluble in water and the usual solvents.

Phenoxyethylorthobenzoicsulphinide,



$$C_6H_4{<}\genfrac{}{}{0pt}{}{CO}{SO_2}{>}N\cdot CH_2\cdot CH_2\cdot OPh,$$

crystallises in glistening cubes, and melts at 81—82°. It is insoluble in water and cold alcohol, but readily soluble in benzene, acetic acid, and hot alcohol. When warmed with sodium ethoxide, it is hydrolysed to *phenoxyethylorthoamidosulphobenzoic acid*, melting at 139°.

This acid, when heated with concentrated hydrochloric acid for several hours, is partially reconverted into phenoxyethylbenzoicsulphinide; orthosulphobenzoic acid and phenoxyethylamine hydrochloride (Schmidt, Abstr., 1890, 372) are also formed.

Picrylorthobenzoicsulphinide, $C_6H_4{<}\genfrac{}{}{0pt}{}{CO}{SO_2}{>}N\cdot C_6H_2(NO_2)_3$, crystallises in glistening, yellow cubes, melts at 262°, and is soluble in hot acetic acid. It is decomposed by both sodium ethoxide and hydrochloric acid, yielding picric acid and orthobenzoicsulphinide.

J. J. S.

Action of Certain Alcohols on *asym*-Metadiazoxylenesulphonic Acid. By WILLIAM B. SHOBER and HERMAN E. KIEFER (*Amer. Chem. J.*, 1897, i, 381—393).—Xylidinesulphonic acid was prepared by sulphonating α-xylidine, and diazotised by mixing it into a paste with water, passing nitrous fumes in until all had dissolved, and adding alcohol; or by passing nitrous fumes into a cooled suspension of the acid in alcohol. When it is boiled with methylic, ethylic, or propylic alcohols, either under atmospheric pressure or under a pressure of 400—900 mm. of mercury, the diazosulphonic acid always yields a little xylenesulphonic acid, but the main product is an alkoxyxylenesulphonic acid, $OR\cdot C_6H_2Me_2\cdot SO_3H$ [$OR:Me_2:SO_3H = 4:1:3:6$]. Metamethoxyxylenesulphonic acid yields *potassium*, $C_9H_{11}SO_4K + \frac{1}{2}H_2O$; *barium*, $(C_9H_{11}SO_4)_2Ba + 4H_2O$, and *copper*, $(C_9H_{11}SO_4)_2Cu + 4H_2O$, salts, and an *amide* melting at 190°. Propoxyxylenesulphonic acid yields *barium*, $(C_{11}H_{15}SO_4)_2Ba + 3H_2O$; *potassium*, $C_{11}H_{15}SO_4K + H_2O$, and *zinc* $(C_{11}H_{15}SO_4)_2Zn + 5H_2O$, salts, and an *amide* melting at 146°. These salts are yellow, except that the copper salt is green when hydrated. When the methoxyxylenesulphonamide is oxidised with permanganate, it yields two products; one, formed in small amount, melts at 270—275° and contains no nitrogen, but 34·16 per cent. of carbon; the other melts at 236—238°, and is *methoxysulphaminetoluic acid*, $COOH\cdot C_6H_2Me(OMe)\cdot SO_2\cdot NH_2 + H_2O$; its *barium* $(C_9H_{10}NSO_5)_2Ba + 7H_2O$, and *calcium*, $(C_9H_{10}NSO_5)_2Ca + 5H_2O$, salts were prepared.
C. F. B.

Hydrochlorides of Diphenylhydroxyethylamine Bases. By EMIL ERLENMEYER, jun. (*Ber.*, 1897, 30, 1525—1527).—The author contends that two bases of the formula $OH\cdot CHPh\cdot CH_2\cdot NHPh$ exist, one of which melts at 129—130° and the other at 163°. The salts of the first crystallise from water in monoclinic crystals, and from methylic alcohol in very characteristic hexagonal plates containing methylic alcohol of crystallisation, and efflorescing in the air, whilst the salts of the second crystallise either in the hexagonal or monoclinic systems.
J. F. T.

Formation of Diphenylhydroxyethylamine Bases from Benzaldehyde and from Glycocine. By EMIL ERLENMEYER, jun. (*Ber.*, 1897, 1527—1531).—An explanation is given of the curious formation of diphenylhydroxyethylamine bases from benzaldehyde and from glycocine, a reaction which proceeds at ordinary temperatures.
J. F. T.

Resolution of Isohydrobenzoin into its Active Components. By EMIL ERLENMEYER, jun. (*Ber.*, 1897, 30, 1531).—Isohydrobenzoin is readily resolved into its active constituents on crystallising it from ether, the enantiomorphic crystals can thus be obtained a centimetre long, and can be easily measured. For the lævo-modification the value $a_D = 7° 18'$ was found.
J. F. T.

An Isomeride of Triphenylacrylic Acid, and the Conversion of the One into the Other. By VICTOR MEYER and HERMANN WEIL (*Ber.*, 1897, 30, 1281—1284).—As already stated (Abstr., 1896, i, 146), in the preparation of triphenylacrylic acid from dichlorobenzophenone and methylic phenylacetate, a bye-product is formed, which is evidently a diphenylindone of the formula $C_6H_4\genfrac{<}{>}{0pt}{}{CPh}{CO}CPh$, and it was further mentioned that on fusion with potash this substance is converted into an acid. This acid, which is an isomeride of triphenylacrylic acid, separates from glacial acetic acid in colourless crystals resembling common salt, and melting at 185—186°; it probably has the constitution $CHPh\colon CPh\cdot C_6H_4\cdot COOH$, or a *diphenylorthovinylbenzoic acid*, and is formed by the addition of water to the diphenylindone. Both acids are reconverted into the indone by treatment with zinc chloride, although it is not possible to change the one acid directly into the other. J. F. T.

Some Sulphonic Acids of α-Naphthol. By PAUL FRIEDLÄNDER and R. TAUSSIG (*Ber.*, 1897, **30**, 1456—1463).—The authors have found that many of the sulphonic acids of α-naphthol can be purified by means of their zinc salts, since, when syrupy zinc chloride is added to their moderately concentrated aqueous solutions, the impurities are first precipitated, and then the solid zinc salt. 1-Naphthol-2-sulphonic acid seems to be the only α-naphtholsulphonic acid which is sparingly soluble in moderately concentrated mineral acids.

Zinc 1-naphthol-3-sulphonate crystallises in long, faintly pink needles. 1-Naphthol-4-sulphonic acid is best purified by means of its *zinc* salt, which crystallises in rhombic tablets containing 8½ mols. H_2O. The *sodium* salt crystallises in prisms. The product of the action of the calculated amount of fuming sulphuric acid on naphthol seems to be 1-naphthol-2-sulphonic acid (compare Baum, Patent B 4197 of 30th June, 1883; Claus and Oehler, *Ber.*, **15**, 312; Claus and Knyrim, *Ber.*, **18**, 1824).

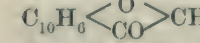
Zinc 1-naphthol-4′-sulphonate crystallises in long, lanceolate needles. When sodium nitrite is added to its solution in hydrochloric acid, *2-nitroso-1-naphthol-4′-sulphonic acid* is formed, crystallising in long, yellow, fascicular needles.

When 1-hydroxy-2-naphthol-4 : 2′-disulphonic acid is heated at 140—145° with moderately concentrated sulphuric acid, it is converted into *1-hydroxy-2-naphthol-2′-sulphonic acid*, which crystallises in sparingly soluble, slender, white needles, and separates from a hot concentrated solution in a very characteristic gelatinous mass of microscopic needles; its aqueous solution is coloured indigo-blue by ferric chloride. The *barium* salt, $[C_{10}H_5(OH)(COOH)SO_3]_2Ba$, forms very sparingly soluble white needles. When the acid is heated with water at 120°, it loses carbonic anhydride and forms 1-naphthol-2′-sulphonic acid, as a hygroscopic, crystalline mass, which gives a brownish-violet coloration with ferric chloride. The *zinc* salt forms stellate groups of large, readily soluble needles. It combines with 1 molecule of paradiazonitrobenzene in acid solution, and with 2 molecules in alkaline solution.

The acid obtained by Gürke and Rudolph (German Patent 38281) is identical with that obtained by Freund (German Patent 27346), and has the constitution of a 1-naphthol-3 : 3′-disulphonic acid, since both of these are converted by heating with ammonia into the same 1 : 3-naphthylendiamine-3-sulphonic acid.

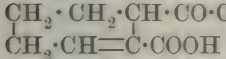
1-Naphthol-2 : 4 : 2′-trisulphonic acid is characterised by its *barium* salt, which separates in very slender, glistening crystals, which are very difficult to redissolve even in boiling water. The sulphonic group in the position 4 is very easily removed by the action of sodium amalgam or sodium nitrite. This acid appears to be formed by much more dilute sulphuric acid than has hitherto been supposed, acid of 66° B. converting at least a seventh of the naphthol used into this acid at 125°. A. H.

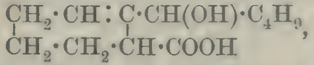
Naphthoketocoumarin and its Condensation Products. By G. Ullmann (*Ber.*, 1897, **30**, 1466—1470).—2 : 1-Acetylnaphthol (Friedländer, Abstr., 1895, i, 668) is not readily acetylated, the best yield of the *acetate*, $C_{10}H_6Ac·OAc$, is obtained when the acetylnaphthol (1 part) is heated with acetic anhydride (3—3½ parts) and anhydrous sodium acetate (1 part) until its alcoholic solution no longer gives a green colour with ferric chloride. It crystallises from its alcoholic solution in long, brownish needles, melts at 103·5°, and is readily soluble in the usual solvents. It yields no coloration with ferric chloride, and is readily hydrolysed by alkalis. 2 : 1-*Acetylnaphthylic benzoate*, $C_{10}H_6Ac·OBz$, also crystallises in long, brownish needles, and melts at 96·5°.

Bromine readily reacts with an acetic acid solution of acetylnaphthylic acetate, even when the two are used in molecular proportion, yielding a 2-*bromacetylbromo*-1-*naphthol*, $OH·C_{10}H_5Br·CO·CH_2Br$, which crystallises in yellowish needles and melts at 136·5°; bromine reacts with a benzene solution of acetylnaphthylic acetate, forming *bromacetylbromonaphthylic acetate*, $OAc·C_{10}H_5Br·CO·CH_2Br$. This crystallises in colourless needles, melts at 124°, and is fairly readily soluble in alcohol. Both compounds are decomposed by sodium hydroxide, yielding red solutions, and both form the same condensation products with aldehydes. 2 : 1-*Bromacetylnaphthol*, obtained by the action of bromine (1 mol.) on a solution of acetylnaphthol in dry carbon bisulphide, crystallises in colourless plates and melts at 77—87°, but the compound cannot be obtained in a pure form. The naphthol, when dissolved in carbon tetrachloride, reacts with bromine, yielding a monobromo-derivative, $OH·C_{10}H_6·CO·CH_2Br$, melting at 124·5 together with other products. When the finely-divided monobromoderivative is warmed for a short time with caustic soda (1 mol.) and hydrochloric acid is then added, a precipitate of *naphthoketocoumarin*,  $C_{10}H_6<\genfrac{}{}{0pt}{}{O}{CO}>CH_2$, is obtained. When recrystallised from water, this melts at 91—92°; it is but slowly volatile with steam, dissolves readily in ether, and only sparingly in alcohol. On warming with Fehling's solution, it yields a magenta-red solution from which a violet-red precipitate is thrown down.

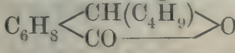
Naphthoketocoumarin (2 parts) reacts with an alcoholic solution of protocatechuic aldehyde (1 part) in the presence of concentrated hydrochloric acid, yielding a yellow, crystalline *naphthoflavone* which melts and decomposes at 240°. It is readily purified by means of its sodium salt, which is precipitated on adding strong sodium hydroxide to its aqueous solution. The *methylenic ether* of this compound is obtained by the condensation of naphthoketocoumarin with piperonal; it crystallises in yellow needles, is sparingly soluble in the usual solvents, but dissolves more readily in acetic acid or amylic alcohol. 2 : 1-Dibromacetylnaphthol also reacts with piperonal, yielding a condensation product which crystallises in yellow needles. The author has not been successful in preparing the brominated or chlorinated acetylnaphthols by the action of brom- or chlor-acetic acid on α-naphthol in the presence of zinc chloride. With phosphorus oxychloride, a *chloracetyl* compound melting at 48° was obtained.

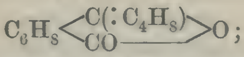
J. J. S.

Odorous Constituents of Oil of Celery. By GIACOMO L. CIAMICIAN and PAUL G. SILBER (*Ber.*, 1897, **30**, 1419—1424. Compare this vol., i, 291).—The authors have definitely established the formula  $\begin{matrix}CH_2\cdot CH_2\cdot CH\cdot CO\cdot C_4H_9\\ CH_2\cdot CH{=}C\cdot COOH\end{matrix}$ for sedanonic acid, which is therefore orthovaleryl-Δ^1-tetrahydrobenzoic acid; sedanolic acid, on the other hand, is orthohydroxyamyl-Δ^5-tetrahydrobenzoic acid,

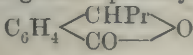


$$\begin{matrix}CH_2\cdot CH : C\cdot CH(OH)\cdot C_4H_9,\\ CH_2\cdot CH_2\cdot CH\cdot COOH\end{matrix}$$

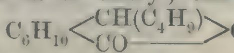
the experiments on which these conclusions are based being described in the following abstracts. The odoriferous constituents are sedanolide,  $C_6H_8<\begin{matrix}CH(C_4H_9)\\ CO\end{matrix}>O$, and an anhydride of sedanonic acid,



$$C_6H_8<\begin{matrix}C(:C_4H_8)\\ CO\end{matrix}>O;$$

the former substance is butylphthalide, and it is interesting to notice that hydrogenised phthalylisopropylidene, which probably has the constitution  $C_6H_4<\begin{matrix}CHPr\\ CO\end{matrix}>O$, has an odour which suggests celery oil.

M. O. F.

Sedanonic Acid. By GIACOMO L. CIAMICIAN and PAUL G. SILBER (*Ber.*, 1897, **30**, 1424—1427. Compare the preceding abstract).—*Orthohydroxyamylhexahydrobenzoic acid* (2^1-*pentylolcyclohexanemethylic acid*), $COOH\cdot C_6H_{10}\cdot CH(OH)\cdot C_4H_9$, is prepared by reducing sedanonic acid with sodium and alcohol, and crystallises in needles; it is identical with the product from sedanolic acid, and after repeated crystallisation from ethylic acetate melts at 131°. When the substance is treated with boiling acetic chloride, and the agent evaporated, a colourless oil is produced having the odour of oil of celery; this substance is probably hexahydrobutylphthalide,  $C_6H_{10}<\begin{matrix}CH(C_4H_9)\\ CO\end{matrix}>O$, and yields the acid when hydrolysed with caustic alkali.

Cold solutions of sedanonic acid are indifferent towards sodium amalgam; when heated with this agent, however, the *acid* $C_{12}H_{20}O_3$ is produced, yielding an amorphous *silver* salt.

When sedanonic acid is oxidised in alkaline solution with potassium permanganate, oxalic, glutaric, and normal valeric acids are produced.

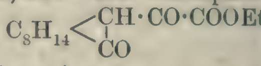
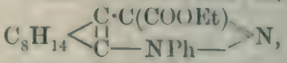
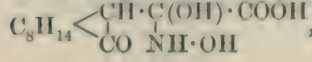
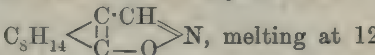
M. O. F.

Sedanolic Acid and Sedanolide. By GIACOMO L. CIAMICIAN and PAUL G. SILBER (*Ber.*, 1897, **30**, 1427—1433. Compare the foregoing abstracts).—*Orthohydroxyamylbenzoic acid* (2^1-*Pentylolphenmethylic acid*), $COOH\cdot C_6H_4\cdot CH(OH)\cdot C_4H_9$, is obtained by oxidising sedanolide in alkaline solution with potassium permanganate, and separates in aggregates of small needles on adding petroleum to the ethereal solution; it melts at 71—72°, and readily undergoes conversion into the anhydride, *butylphthalide*, which has the odour of celery oil, and boils at 177—178° under a pressure of 15 mm. Phenylglyoxylcarboxylic acid is another product of the oxidation of sedanolic acid; the acidic filtrate from orthohydroxyamylbenzoic acid contains the products of ring hydrolysis, oxalic, succinic, and normal valeric acids.

Hydrosedanolidecarboxylic acid, $C_{13}H_{20}O_4$, is obtained by the action of alcoholic potassium cyanide on sedanolide, and hydrolysing the nitrile produced (compare Bredt and Kallen, this vol., i, 154); the *silver* salt is amorphous.

Reduction of sedanolic acid with sodium and alcohol gives rise to orthohydroxyamylhexahydrobenzoic acid, obtained in the same way from sedanonic acid (foregoing abstract).

M. O. F.

Action of Ethylic Oxalate on Camphor. II. By J. BISHOP TINGLE (*Amer. Chem. J.*, 1897, **19**, 393—409. Compare Trans., 1890, 652).—Ethylic camphoroxalate,  $C_8H_{14}<\begin{matrix}CH\cdot CO\cdot COOEt\\ |\\ CO\end{matrix}$, is best prepared by dissolving camphor ($1\frac{1}{2}$ mol.) and ethylic oxalate (1 mol.) in light petroleum, adding sodium wire (1 atom), boiling for about half an hour in a reflux apparatus, and allowing to remain for 24 hours; the yield is about 75 per cent. of the theory, and 17 per cent. of the acid itself is obtained besides. It will not yield a copper salt, and appears to have no acid properties; it is readily hydrolysed by aqueous sodium hydroxide in the cold; when heated, it decomposes for the most part into alcohol and the acid, no doubt by the agency of traces of water, and the remainder is further decomposed into camphor and ethylic hydrogen oxalate, which is yet further resolved into ethylic formate and carbonic anhydride. Its phenylhydrazone, when purified by recrystallisation, melts at 212°, and not at 187—188° as previously stated; by mixing it with half the amount of alcohol necessary for complete solution, and passing in hydrogen chloride at 0° until all has dissolved, *ethylic camphylphenylpyrazolecarboxylate*,  $C_8H_{14}<\begin{matrix}C\cdot C(COOEt)\\ \|\\ C—NPh—\end{matrix}>N$, melting at 114°, is obtained (the same condensation takes place at a higher temperature under the influence of acetic anhydride); this substance is readily hydrolysed by alcoholic potash to the free *acid*, which melts at 197° when dry. Camphoroxalic acid is found to crystallise in hexagonal forms, like those of quartz; with a large excess of hydroxylamine, it yields an additive *compound*,  $C_8H_{14}<\begin{matrix}CH\cdot C(OH)\cdot COOH\\ |\quad\ |\\ CO\ \ NH\cdot OH\end{matrix}$, which melts and decomposes at 146·5°, and, when heated with acetic anhydride and acetic acid, yields *camphylisoxazole*,  $C_8H_{14}\left<\begin{array}{c}C\cdot CH\\ \|\\ C{-}O\end{array}\right>N$, melting at 124—125°.

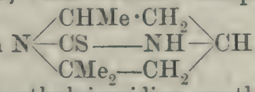
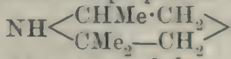
C. F. B.

Pyrethrin, the Active Principle of the Root of Anacyclus Pyrethrum Dec. By August Schneegans (*Chem. Centr.*, 1896, ii, 945—946; from *Pharm. Zeit.*, **41**, 668).—In order to prepare pure pyrethrin, the triturated root is boiled several times with alcohol, and the extract, after driving off the alcohol, is treated with absolute alcohol, whereby a large quantity of a grey, tasteless tar is separated. With alcoholic lead acetate solution, a yellow precipitate is formed; this is removed, the filtrate freed from lead by hydrogen sulphide, evaporated, and the reddish-yellow syrup freed from tar by dissolving in ether and evaporating to dryness with addition of milk of lime and sand. The solid powdered mass is extracted with light petroleum and the light yellow solution so obtained freed from a brown, tasteless oil by shaking with sodium hydroxide solution, evaporated and finally crystallised by drying over sulphuric acid in a vacuum. By draining and washing with a little ether, the crystals may be cleansed from the adherent dark oil. *Pyrethrin* forms white, clustered needles, melts at 45°, and has an extremely burning taste. It is very easily soluble in absolute alcohol, ether, benzene, glacial acetic acid, chloroform, and carbon bisulphide, easily soluble in light petroleum, and insoluble in water, dilute acids, and alkalis. It forms a yellow solution in concentrated sulphuric acid which changes at once to red. Its solution in glacial acetic acid, on addition of sodium nitrite, turns red after a little time.

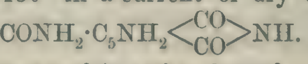
E. W. W.

Action of Acetic Acid and Zinc Dust on 2:5-Dimethylpyrroline. By Carlo U. Zanetti and A. Cimatti (*Ber.*, 1897, **30**, 1588—1590).—When 2:5-dimethylpyrroline is reduced with zinc dust in acetic acid solution, the base, $C_{12}H_{17}N$, is obtained; it forms long, colourless needles melting at 74—75°, and becomes red on exposure to air. The *hydrochloride* and *picrate* melt at 242—244° and 200° respectively, and the *platinochloride* crystallises in yellow needles melting at 241—242°.

M. O. F.

Existence of Condensation Rings with Para-Linkage. By Albert Ladenburg (*Ber.*, 1897, **30**, 1586—1588. Compare Harries, this vol., i, 293).—The constitution  $N\left<\begin{array}{l}CHMe\cdot CH_2\\ CS{-}{-}NH\\ CMe_2{-}CH_2\end{array}\right>CH$ having been ascribed by Harries to α-amidotrimethylpiperidine eso-thiocarbamide (*loc. cit.*), the author points out that the properties of the substance are consistent with the formula  $NH\left<\begin{array}{l}CHMe\cdot CH_2\\ CMe_2{-}CH_2\end{array}\right>CH\cdot N{:}CS$; he is of opinion that there is at present no ground for representing compounds as having para-linkage.

M. O. F.

Etherification of 2:3:4-Pyridinetricarboxylic Acid. By Otto Rint (*Monatsh.*, 1897, **18**, 223—243).—It is not possible to obtain more than a diethylic salt, either by saturating an alcoholic solution of the acid with gaseous hydrogen chloride, or by acting on the acid with excess of phosphoric chloride and treating the product with alcohol; or by the action of sodium ethoxide and sodium ethylsulphate, or of phosphoric chloride and alcohol on the diethylic salt. The ethylic salt described by Dobbie and Ramsay (Trans., 1879, 189) and Roser (*Annalen*, 1886, **234**, 125) was in reality the diethylic salt. *Dimethylic* and *diethylic* 2 : 3 : 4-*pyridinetricarboxylates* [probably $COOH:(COOEt)_2 = 2:3:4$], are best prepared by saturating with gaseous hydrogen chloride a 10 per cent. solution of the acid in the absolute alcohol, and heating eventually to boiling; the *hydrochloride* of the salt separates out as the solution cools. The ethylic salt is the more easily prepared. The methylic and ethylic salts melt respectively at 165—166° and 118° (uncorr.); they are best prepared from the hydrochlorides, which melt at 177—178° and 142°, by boiling the latter with benzene in a current of carbonic anhydride until all the hydrogen chloride has been driven off. In the alcoholic mother liquor from the hydrochloride of the ethylic salt, diethylic cinchomeronate (3 : 4-pyridinedicarboxylate) was detected; the same substance is formed when diethylic pyridinetricarboxylate is heated for 24 hours at 150—160°, or for 6—7 hours with saturated alcoholic hydrochloric acid at 210° in a sealed tube, carbonic anhydride being evolved of course. When diethylic pyridinetricarboxylate is heated for 5 hours with ethylic iodide in a sealed tube at 110°, the iodide of ethylic ethylapophyllenate, $C_5H_3NEtI(COOEt)_2$ [$Et:I:(COOEt)_2 = 1:1:3:4$], (Blumenfeld, Abstr., 1896, i, 60) is formed. When it is allowed to remain for several days with aqueous ammonia saturated at $-10°$, it forms *ammonium pyridinetricarbodiamate*, $COONH_4 \cdot C_5(NH_2) \vdots (CONH_2)_2$; this can be recrystallised from cold water, but on one occasion the *diammonium monomate*, $C_5NH_2(COONH_4)_2 \cdot CONH_2$, resulted from this process. These substances give *triammonium pyridinetricarboxylate*, $C_5NH_2(COONH_4)_3$, when boiled with water, and the first mentioned, when heated at 120—130° in a current of dry carbonic anhydride, yields the *amidimide*,  $CONH_2 \cdot C_5NH_2 {<}\begin{smallmatrix}CO\\CO\end{smallmatrix}{>} NH$. All of these substances decompose without melting when heated. C. F. B.

2 : 6-Diphenylpyridine and 2 : 6-Diphenylpiperidine. By Carl Paal and Karl Demeler (*Ber.*, 1897, **30**, 1499—1504).—After it had been shown that the 2 : 6-diphenylpyridine prepared from diphenacylmalonic and diphenacylacetic acids was identical with the compound obtained by Scholtz from the oxime of cinnamylideneacetophenone (Abstr., 1895, i, 562), attempts were made to convert it into some well-known derivative of pyridine, and with this object it was subjected to the action of concentrated nitric acid. Two isomeric dinitro-derivatives were produced, namely, *α-dinitro* 2 : 6-*diphenylpyridine*, $C_5NH_3(C_6H_4 \cdot NO_2)_2$ [$= 2:6$], crystallising from glacial acetic acid in light yellow needles melting at 210—220°, and *β-dinitro-*2 : 6-*diphenylpyridine* crystallising from dilute alcohol in nodular masses melting at 110—111°.

On reducing the α-dinitro-compound with tin and hydrochloric acid, the corresponding *a-diamido*-derivative is produced, which forms silky needles melting at 75—76°, and yields a *hydrochloride*, $C_{17}H_{15}N_3,3HCl$, crystallising in groups of needles, and decomposing at 300°; the platinochloride and aurochloride are unstable.

Dipicolinic acid [pyridine-2 : 6-dicarboxylic acid], $C_5NH_3(COOH)_2$, $[(COOH)_2 = 2 : 6]$, is formed when the free diamido-base is oxidised by potassium permanganate; it slowly separates from its aqueous solutions in white needles melting at 226—227°.

2 : 6-*Diphenylpiperidine*, $C_5NH_9Ph_2$, formed when diphenylpyridine is reduced in alcoholic solution with sodium, can be purified by recrystallising its hydrochloride. The base crystallises in colourless plates melting at 69°, the *hydrochloride* melts at 315—316°, the *platinochloride* at 206—207°, and the *aurochloride* at 202°. J. F. T.

Piperonylpicoline. By J. Thiemich (*Ber.*, 1897, **30**, 1578—1582).—*Piperonylpicoline*, $C_5NH_4\cdot CH\colon CH\cdot C_6H_3\colon O_2CH_2$, is obtained by heating picoline with piperonaldehyde (1 mol.) and a small quantity of zinc chloride in a sealed tube at 190—200° during 6 hours; it melts at 109°, and separates from alcohol in small, lustrous crystals, which exhibit feeble blue fluorescence. The *hydrochloride* becomes brown at 260—261°, and melts at 265—267°, when it decomposes; the *picrate* forms dark yellow needles, sinters at 214°, and melts at 217°. The *platinochloride* melts and becomes black at 199—200°, the *aurochloride* is unstable, and the *mercurochloride*, which is yellow, becomes colourless in light, and melts at 239—240°; the *dibromide* is a white powder which readily decomposes.

Piperonylpipecoline, $C_5NH_9\cdot CH_2\cdot CH_2\cdot C_6H_3\colon O_2CH_2$, is prepared by reducing the foregoing base with sodium and amylic alcohol; it is an odourless oil having alkaline action on litmus, and boils at 180—182° under a pressure of 100 mm. The *hydrochloride* crystallises in colourless, silky needles, and melts at 177°. The *picrate* and *platinochloride* melt at 178° and 189° respectively, and the *mercurochloride* is an oil which solidifies slowly. M. O. F.

2′-3′-Dimethylquinoline. By Ernst Fraenkel (*Chem. Centr.*, 1896, ii, 877; from *Diss. Freiburg*).—2′-3′-Dimethylquinoline, $C_9NH_5Me_2$, which melts at 67°, was prepared according to the description of Rhode and of Friedländer and Eliasberg with a view of investigating the bromination of a 3′-substituted quinoline and obtaining a 2′-3′quinolinedicarboxylic acid. The compound with methylic iodide which melts at 218°, after decomposition with potassium hydroxide, is converted into the methylic chloride compound by the action of hydrochloric acid. By allowing the products of the reaction to remain exposed to the air, or by oxidation with an alkaline solution of potassium ferricyanide, an alkylidene base, $C_9H_5Me_2N\colon CH_2$, is probably first formed from the quaternary base, $C_9H_5Me_2NMeOH$, originally produced, and then changes into 1′ : 2′ : 3′-*trimethyl-4-quinolone*, $C_9NH_4Me_3O$, which melts at 80°. Dyes are also produced. By oxidation of the dimethylquinoline with chromic acid, no dicarboxylic acid is formed, but only quinaldine-3-carboxylic acid which melts at 235—238°, whilst by oxidation with potassium permanganate only oxalic acid, carbonic anhydride, and ammonia are formed. Attempts to brominate 2′-3′-dimethylquinoline directly failed; by nitration, however, a mononitro-compound results which melts at 95°, and is probably 4-nitro-2′-3′-dimethylquinoline. The amido-compound obtained from this by reduction forms salts with one equivalent of acid. The acetyl derivative melts at 190—195°, and the methylic iodide compound decomposes at 220°. On bromination, the amido-compound yields a dibromo-derivative, probably 1 : 3-dibromo-4-amido-2′-3′-dimethylquinoline, $C_9NH_2Me_2Br_2\cdot NH_2$, which melts at 154°. From 2′ : 3′-dimethylquinoline two sulphonic acids can be prepared.

E. W. W.

Action of Ethylic Oxalate and Sodium Ethoxide on Quinaldine. By WILHELM WISLICENUS (*Ber.*, 1897, **30**, 1479—1480).—Dry sodium ethoxide (from 3·9 grams of sodium) and ethylic oxalate (28 grams) were dissolved in ether and then mixed with 25 grams of quinaldine. At the end of several weeks, the mixture had solidified to a dark red, gelatinous mass in which yellow crystals of *sodium quinaldineoxalate* [*quinolylpyruvic acid*] were embedded. When this salt was carefully acidified with sulphuric acid, the free acid, $C_9NH_6\cdot CH_2\cdot CO\cdot COOH$, was obtained as a yellow precipitate. After recrystallisation from water, it forms beautiful, red needles with a slight blue fluorescence, and decomposes above 170° without melting. It is readily soluble in hot water, its alcoholic solution gives a brownish-red coloration with ferric chloride, and it is partially decomposed into quinaldine and oxalic acid when boiled with alkalis (compare E. Erlenmeyer, jun., Abstr., 1889, 991).

J. J. S.

Derivatives of Piperazine. By W. HERZ (*Ber.*, 1897, **30**, 1584—1586).—When piperazine is heated with concentrated hydrochloric acid in sealed tubes at temperatures between 100° and 250°, no elimination of ammonia takes place; concentrated sulphuric acid also yields negative results, the sole product being piperazine *sulphate*, which is readily soluble in water. The *acetate* decomposes in air, and the *diacetyl* derivative crystallises in colourless plates, and melts at 134°. The carbon bisulphide *compound* sublimes at 212°, and is insoluble in ether, benzene, chloroform, and water; mercuric chloride and lead salts do not eliminate hydrogen sulphide, as in the case of certain products of condensation of amidopiperidine (this vol., i, 295).

Piperazine yields a colourless *compound*, $(C_4H_9N_2)_2CO,4HCl$, when heated with phosgene in sealed tubes at 50°; it dissolves readily in water, is sparingly soluble in other media, becomes brown at 200°, and blackens at 270°.

Benzaldehyde combines with piperazine, forming a *compound* which decomposes in the desiccator. The formaldehyde *compound*,

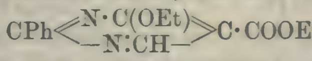
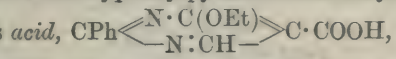
$$C_4H_{10}N_2,2CH_2O,$$

is colourless when dry, and becomes brown at 170°, finally sintering at 225°, when it blackens.

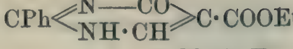
M. O. F.

Pyrimidines. By SIEGFRIED RUHEMANN and A. S. HEMMY (*Ber.*, 1897, **30**, 1488—1492. Compare this vol., i, 376).—An almost theoretical yield of ethylic phenylpyrimidonecarboxylate may be obtained when a similar method to that used for the preparation of ethylic pyroxoloncarboxylate (this vol., i, 445) is adopted.

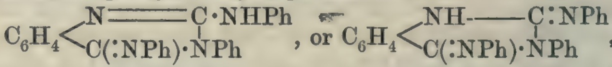
Its *platinochloride*, $(C_{13}H_{12}N_2O_3)_2,H_2PtCl_6$, crystallises in yellowish-red prisms, which are decomposed by water. The *acid* obtained by the hydrolysis of the ethylic salt has both basic and acidic properties; it readily dissolves in concentrated hydrochloric acid, and is thrown down again on the addition of water.

Two ethylic ethoxyphenylpyrimidinecarboxylates are obtained by the action of ethylic iodide on the silver salt of the above-mentioned ethereal salt. The silver salt is most readily obtained by dissolving ethylic phenylpyrimidonecarboxylate in alcohol, and adding alcoholic solutions of ammonia and silver nitrate. The two ethylic salts are best separated by means of ether; the one which is present in much greater quantity,  $\mathrm{CPh}{<}\genfrac{}{}{0pt}{}{\mathrm{N\cdot C(OEt)}}{\mathrm{-N{:}CH-}}{>}\mathrm{C\cdot COOEt}$, is readily soluble in ether, and crystallises from alcohol in colourless prisms melting at 58—59°. The amount of the second ethylic salt was too small for further investigation. When the ethylic salt melting at 58—59° is boiled with concentrated hydrochloric acid, it yields phenylpyrimidonecarboxylic acid; boiling alcoholic potash, on the other hand, yields a mixture of this acid with ethoxyphenylpyrimidinecarboxylic acid. These two acids are easily separated by means of absolute alcohol, which dissolves the ethoxyphenylpyrimidinecarboxylic acid with great readiness. This *acid*,  $\mathrm{CPh}{<}\genfrac{}{}{0pt}{}{\mathrm{N\cdot C(OEt)}}{\mathrm{-N{:}CH-}}{>}\mathrm{C\cdot COOH}$, which is isomeric with ethylic phenylpyrimidinecarboxylate, crystallises in colourless needles, melts at 193—194°, and is readily soluble in alkalis or concentrated hydrochloric acid. Addition of silver nitrate to its ammoniacal solution precipitates a white, insoluble, and somewhat stable *silver* salt. The authors have attempted to prepare an alkylic derivative of ethylic phenylpyrimidonecarboxylate, in which the alkylic group should be attached to nitrogen, using a method similar to that employed by Fischer in the uric acid series (this vol., i, 267). On warming the ethylic salt with normal sodium hydroxide and methylic iodide, however, they found that the greater part of the ethylic salt was hydrolysed. A small quantity of a compound melting at 165° was obtained, but the quantity was too small to investigate.

When phenylpyrimidonecarboxylic acid is heated at 265°, it loses carbonic anhydride and yields *phenylpyrimidone*, $C_{10}H_8N_2O$, which distils at 260—263° under a pressure of about 30 mm. It crystallises from alcohol in glistening needles, melts at 207—208°, and is readily soluble in hot water and also in ammonia; from the latter solution, a *silver* salt, $C_{10}H_7AgN_2O$, may be obtained. Phenylpyrimidone also possesses basic properties, since it is soluble in concentrated hydrochloric acid and yields a *platinochloride*, $(C_{10}H_8N_2O)_2,H_2PtCl_6$, crystallising in yellowish-red prisms. J. J. S.

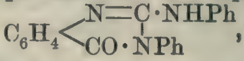
Formation of Pyrimidones. By C. WOLF (*Ber.*, 1897, 30, 1564—1565).—Although phenylhydrazine reacts with ethylic dicarboxyglutaconate, yielding alcohol, ethylic malonate, and ethylic phenylpyrazolonecarboxylate (Ruhemann and Morrell, Trans., 1892, 61, 794) benzamidoxime and ethylic dicarboxyglutaconate give rise to ethylic phenylpyrimidonecarboxylate,  $\mathrm{CPh}\left<\begin{matrix}\mathrm{N{-}{-}CO}\\ \mathrm{NH\cdot CH}\end{matrix}\right>\mathrm{C\cdot COOEt}$ (Ruhemann, this vol., i, 376). M. O. F.

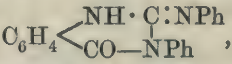
Action of Aluminium Chloride on the Chlorides of Carbodiphenylimide: Synthesis of Anilidoquinazolines. By HERBERT N. McCOY (*Ber.*, 1897, 30, 1682—1693. Compare this vol., i, 422).—*2′-Anilido-3′-phenyl-4′-phenylimidodihydroquinazoline*, or *2′ : 4′-diphenylimido-3′-phenyltetrahydroquinazoline*,



$$\mathrm{C_6H_4}\left<\begin{matrix}\mathrm{N{=}{=}C\cdot NHPh}\\ \mathrm{C(:NPh)\cdot NPh}\end{matrix}\right., \text{ or } \mathrm{C_6H_4}\left<\begin{matrix}\mathrm{NH{-}{-}C:NPh}\\ \mathrm{C(:NPh)\cdot NPh}\end{matrix}\right.,$$

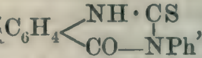
is obtained by saturating a solution of carbodiphenylimide in benzene with hydrogen chloride, diluting the liquid with carbon bisulphide, and heating it in a reflux apparatus with aluminium chloride. It forms rhombic plates melting at 184°, and when heated with aniline at 110—160° yields an isomeric modification which crystallises in needles and melts at 171°; crystallisation from boiling alcohol also converts the compound melting at 184° into the isomeride.

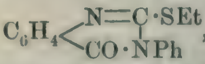
2′-Anilido-3′-phenyl-4′-ketodihydroquinazoline, or *2-phenylimido-3′-phenyl-4′-ketotetrahydroquinazoline*,  $\mathrm{C_6H_4}\left<\begin{matrix}\mathrm{N{=}C\cdot NHPh}\\ \mathrm{CO\cdot NPh}\end{matrix}\right.$, or

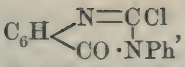


$$\mathrm{C_6H_4}\left<\begin{matrix}\mathrm{NH\cdot C:NPh}\\ \mathrm{CO{-}NPh}\end{matrix}\right.,$$

is obtained by hydrolysing the foregoing compounds with alkalis, aniline being simultaneously produced; it crystallises from boiling alcohol in colourless needles, and melts at 163°. When further hydrolysed by concentrated hydrochloric acid in sealed tubes at 160—180°, it yields 3′-phenyl-2′ : 4′-diketotetrahydroquinazoline, which melts at 272° (Paal, Abstr., 1894, i, 332, and Busch, Abstr., 1895, i, 307).

2′-Thio-3′-phenyl-4′-ketotetrahydroquinazoline,  $\mathrm{C_6H_4}\left<\begin{matrix}\mathrm{NH\cdot CS}\\ \mathrm{CO{-}NPh}\end{matrix}\right.$, is obtained by heating anthranilic acid with phenylthiocarbimide (1 mol.) and aqueous caustic soda (1 mol.), sufficient alcohol being added to yield a clear solution; orthophenylthioureidobenzoic acid is first formed, and then undergoes condensation. The thio-compound dissolves readily in alkalis, and is precipitated by carbonic anhydride, but is scarcely soluble in sodium carbonate; it crystallises from a mixture of alcohol and acetone in colourless, rectangular plates, and melts above 300° without decomposing. Oxidation with potassium permanganate converts the substance into 3′-phenyl-2′ : 4-diketotetrahydroquinazoline. When heated with aniline in sealed tubes at 300°, it yields 2′ : 4′-phenylimido-3′-phenyltetrahydroquinazoline.

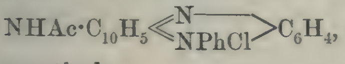
2′-Ethylthio-3′-phenyl-4′-ketodihydroquinazoline,  $\mathrm{C_6H_4}\left<\begin{matrix}\mathrm{N{=}C\cdot SEt}\\ \mathrm{CO\cdot NPh}\end{matrix}\right.$, is prepared from the foregoing compound by the action of ethylic iodide in presence of alcoholic potash, and crystallises in colourless needles melting at 114°. Aniline at 300° converts it into 2′-phenylimido-3′-phenyl-4′-ketodihydroquinazoline.

2′-Chloro-3′-phenyl-4′-ketodihydroquinazoline,  $C_6H\!<\!\begin{array}{l}N{=}CCl\\ CO\cdot NPh\end{array}$, is obtained when chlorine is passed into a solution of thiophenylketotetrahydroquinazoline dissolved in chloroform, forming a colourless oil which crystallises; alkalis convert it into 3′-phenyl-2′ : 4′-diketotetrahydroquinazoline, and aniline gives rise to 2-anilido-3′-phenyl-4′-ketodihydroquinazoline.

2′-Anilido-3′-phenyl-4′-phenylimidodihydroquinazoline is produced when the foregoing chloro-compound is heated with phosphorus oxychloride and phosphorus pentachloride, and after removal of the former, treated with free aniline. M. O. F.

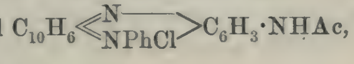
Conversion of Phenylphenazonium into Phenosafranine, and of Nietzki and Otto's Isorosinduline into Naphthophenosafranine. By Friedrich Kehrmann and W. Schaposchnikoff (*Ber.*, 1897, **30**, 1565—1572).—When aqueous ammonia is added to the orange-yellow, alcoholic solution of acetylaposafranine chloride, and the liquid agitated during several hours, the colour changes to intense bluish-violet, and finally becomes magenta-red; the solution then contains monacetylphenosafranine, and on adding hydrochloric acid, heating the liquid, and evaporating, phenosafranine chloride crystallises. It is, therefore, possible to convert phenosafranine through aposafranine into phenazonium, and to regenerate phenosafranine from phenazonium through aposafranine and its acetyl derivative.

The acetyl derivative of isorosinduline chloride (compare Nietzki and Otto, Abstr., 1888, 843) is converted by ammonia into acetylnaphthophenosafranine chloride. Naphthophenosafranine chloride contains $1H_2O$, and forms a bluish-green solution in concentrated sulphuric acid; the platinochloride is red, and the nitrate crystallises in green needles. This change can only be explained on the assumption that acetylrosinduline and acetylisorosinduline have the formulæ,



$$NHAc\cdot C_{10}H_5\!\ll\!\begin{array}{c}N\\ NPhCl\end{array}\!>\!C_6H_4,$$

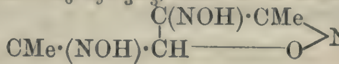
and



$$C_{10}H_6\!\ll\!\begin{array}{c}N\\ NPhCl\end{array}\!>\!C_6H_3\cdot NHAc,$$

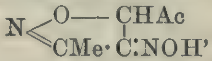
respectively.

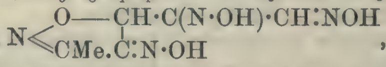
The authors criticise the conclusions of Fischer and Hepp regarding the constitution of methylphenosafranine (this vol., i, 258). M. O. F.

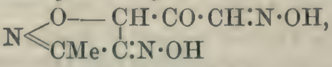
Formation of Isoxazolines from Ketoaldehydes and Isonitrosoketones. By Roland Scholl (*Ber.*, 1897, **30**, 1287—1292).—In the preparation of methylglyoxime from isonitrosoacetone and hydroxylamine hydrochloride, a compound of the formula $C_6H_9N_3O_3$ is obtained as a bye-product, and the formation of substances of this class seems to be general to this reaction. Similarly, compounds, characterised by containing the group N_3O_3 are formed when other isonitrosoketones react with hydroxylamine hydrochloride. The compound formed by the condensation of glyoxal with hydroxylamine hydrochloride can only be a derivative of isoxazoline, that is, 3-oximidomethyl-2-isoxazolonoxime, whilst of the two possible formulæ of the compound $C_6H_9N_3O_3$, that of a 5-methyl-3-oximidoethyl-4-isoxazolonoxime,  $\mathrm{CMe\cdot(NOH)\cdot\overset{\overset{\textstyle C(NOH)\cdot CMe}{|}}{C}H\text{———}O{>}N}$, seems the more probable.

J. F. T.

5-Methyl-3-oximidoethyl-4-isoxazolonoxime. By Roland Scholl and Moritz Baumann (*Ber.*, 1897, **30**, 1292—1313).—After the compound $C_6H_9N_3O_3$, obtained from isonitrosoacetone and hydroxylamine hydrochloride, had been identified as a 5-methyl-3-oximidoethyl-4-isoxazolonoxime, several derivatives of it were prepared, notably by the action of nitrogen tetroxide, nitrogen trioxide, and various strengths of nitric acid.

On treating the dioxime with a mixture of concentrated and fuming nitric acids, a substance is produced corresponding with the formula $C_6H_8N_2O_3$, and evidently formed by the elimination of an oxime group from the dioxime, since, on treatment with hydroxylamine hydrochloride, it again yields the dioxime $C_6H_9N_3O_3$; although this *monoximeketone*,  $\mathrm{N{<}\begin{matrix}O\text{——}CHAc\\ \;|\\ CMe\cdot C{:}NOH\end{matrix}}$, cannot be obtained in a pure condition, it readily forms a *hydrazone*, $C_{12}H_{14}N_4O_2$, crystallising from hot alcohol in yellow crystals melting at 208°.

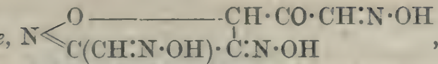
By the action of nitrogen tetroxide on the dioxime suspended in ether, a *trioxime*, $C_6H_8N_4O_4$, evidently *5-methyl-3-dioximidoethyl-4-isoxazolonoxime*,  $\mathrm{N{<}\begin{matrix}O\text{——}CH\cdot C(N\cdot OH)\cdot CH{:}NOH\\ \;|\\ CMe.C{:}N\cdot OH\end{matrix}}$, is produced, which separates in slender, yellow needles containing 1 mol. H_2O, on pouring its solution in hot glacial acetic acid into water, and melts at 221°. By the further action of nitrogen tetroxide on this trioxime, a *substance*, $C_{12}H_{12}N_6O_7$, of unknown constitution is produced, together with a dioxime-ketone, $C_6H_7N_3O_4$; the former is obtained in the form of slender, snow-white needles, melting and decomposing at 267°, on pouring its solution in chloroform into ether, whilst the latter, which is evidently *3-oximidoacetyl-5-methyl-4-isoxazolonoxime*,



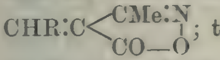
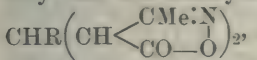
$$\mathrm{N{<}\begin{matrix}O\text{——}CH\cdot CO\cdot CH{:}N\cdot OH,\\ \;|\\ CMe\cdot C{:}N\cdot OH\end{matrix}}$$

separates from hot water in the form of faintly yellow needles melting at 91°. The *sodium* salt forms slender, white needles, and the *silver* salt light yellow needles; hydroxylamine hydrochloride causes the reformation of the trioxime, $C_6H_8N_4O_4$; phenylhydrazine produces a yellow, crystalline *hydrazone*, $C_{12}H_{13}N_5O_3$, melting, with decomposition, at 234°; aniline, a *compound*, $C_{12}H_{14}N_4O_4$, separating from water in long, thick plates; dimethylparaphenylenediamine, a *compound*, $C_{14}H_{17}N_5O_3$, separating from hot alcohol in dark-red, metallic needles, melting, with decomposition, at 206°, and diazobenzene, a *compound*, $C_{12}H_{11}N_5O_4$, separating from hot benzene in dark-red needles, melting, with violent decomposition, at 208°.

The trioxime, $C_6H_8N_4O_4$, is converted, on careful treatment with "green" nitric acid, into a trioxime-ketone. *3-Oximidoacetyl-5-oximido-*

methyl-4-isoxazolonoxime,  $N\!<\!\begin{array}{l}O\text{———————}CH\cdot CO\cdot CH{:}N\cdot OH\\ C(CH{:}N\cdot OH)\cdot C{:}N\cdot OH\end{array}$, which slowly separates from a mixture of chloroform and acetone in glistening, yellow prisms melting and decomposing at about 158°.

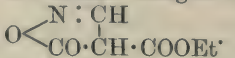
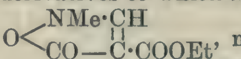
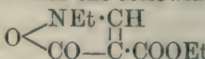
By the action of "green" nitric acid on the dioxime, $C_6H_9N_3O_3$, oxalic acid alone is produced. J. F. T.

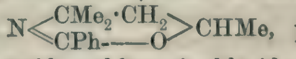
Condensation Products of Methylisoxazolone with Aldehydes and Acetone. By ROBERT SCHIFF and M. BETTI (*Ber.*, 1897, 30, 1337—1343).—It has been already shown (Abstr., 1896, i, 83, and Knoevenagel and Renner, *ibid.*, 189) that benzaldehyde condenses with the oxime of ethylic acetoacetate to form an isoxazolone of the type  $CHR{:}C\!<\!\begin{array}{l}CMe{:}N\\ CO\text{—}O\end{array}$; the most convenient method of preparation is to mix 1 mol. each of a concentrated aqueous solution of hydroxylamine hydrochloride, ethylic acetoacetate, and aniline, and then add 1 mol. of the aldehyde, and a volume of 20 per cent. hydrochloric acid equal to the total volume, and warm on the water bath. The benzaldehyde compound is not so readily decomposed by alkalis as was thought; only half the aldehyde is eliminated, and a compound of the type  $CHR\left(CH\!<\!\begin{array}{l}CMe{:}N\\ CO\text{—}O\end{array}\right)_2$, melting at 145°, remains after this aldehyde has been boiled off; if the mixture is acidified again, without being boiled, recombination takes place, and the isoxazolone is regenerated. Other aldehydes react in the same way, and so does a ketone, acetone, but ketonic acids do not, for ethylic acetoacetate gave the same compound as acetone gives. These isoxazolones, when in aqueous solution, must be regarded as existing in the form of acids,

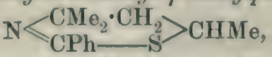
$$COOH\cdot CHR\cdot CMe{:}NOH,$$

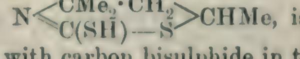
and these are more or less electrolytically dissociated. The acetone derivative, for example, is colourless; its solution in water is, however, yellow, and strongly acid in reaction; if sodium hydroxide is gradually added, the yellow colour deepens at first, reaches a maximum when 1 mol. of soda has been added, and then decreases until it disappears entirely. The action of diazobenzene chloride on the sodium salt of the acetone compound yields the phenylhydrazone of methylisoxazolone melting at 192° (compare Knorr and Reuter, Abstr., 1894, i, 372; melting point there given as 189°); nitrous acid yields a yellow substance melting and decomposing at 174°, probably the analogous *oxime*. The names and melting points of the new substances obtained are *metanitrobenzylidenemethylisoxazolone*, yellowish, 148—149°; *cinnamylidenemethylisoxazolone*, yellow, 175—176°; *piperonylidenemethylisoxazolone*, yellow, 220°; *salicylidenemethylisoxazolone*, yellow, 174—175°; *furfurylidenemethylisoxazolone* (acetic acid used instead of hydrochloric in its preparation), greenish-yellow, solution yellow to red with green fluorescence, 112—113°; *propylidenemethylisoxazolone*, 120—121°. C. F. B.

Isoxazolones. By LUDWIG CLAISEN (*Ber.*, 1887, 30, 1480—1485. Compare Abstr., 1891, 468).—When ethylic ethoxymethylenemalonate (Abstr., 1895, i, 193) is heated with hydroxylamine, a substance

$C_6H_7NO_4$ is obtained to which the author assigns the constitution of *ethylic isoxazolone-β-carboxylate*,  $O<\begin{array}{l}N:CH\\ CO\cdot CH\cdot COOEt\end{array}$. It melts and decomposes at 160—165°, when slowly heated, but if quickly heated, at 183—185°; the compound has the properties of a strong acid and dissolves even in dilute solutions of alkali acetates, and is precipitated unaltered from these solutions on acidification. Ferric chloride gives a deep red coloration, copper acetate yields a bulky, green precipitate, and ammoniacal silver nitrate a white, crystalline precipitate. This *silver* derivative, when heated with methylic or ethylic iodide, yields alkyl derivatives to which the author attributes the following constitutions:  $O<\begin{array}{l}NMe\cdot CH\\ CO—C\cdot COOEt\end{array}$, m. p. 96—97°,  $O<\begin{array}{l}NEt\cdot CH\\ CO—C\cdot COOEt\end{array}$, m. p. 46°. Both are insoluble in dilute alkalis and give no coloration with ferric chloride. When boiled with alkalis, they are decomposed into alkali malonate and carbonate, methylamine or ethylamine being formed at the same time. The formation of the alkyl derivatives by the displacement of the double bond is similar to the reactions observed by Uhlenhuth in the case of the alkyl derivatives of phenyl- and methyl-isoxazolone (this vol., i, 444), and in the formation of antipyrine from phenylmethylpyrazolone and methylic iodide. The paper concludes with a criticism of Ruhemann's formula for isoxazolone (this vol., i, 445), and clearly shows that, although in the alkylic derivatives of isoxazolone the alkylic group is attached to nitrogen, yet it does not follow that an imido-group is present in the original isoxazolone, since the silver salts of numerous compounds, when heated with alkylic iodides, undergo intramolecular decomposition. J. J. S.

Diacetonalkamine. By M. KAHAN (*Ber.*, 1897, **30**, 1318—1326).—The diacetonalkamine for these experiments was prepared from diacetonamine oxalate by Heintz's method. On treatment with fuming hydrobromic acid, it gives the *hydrobromide of γ-bromohexylamine* (2-methyl-2-amino-4-brompentane), $NH_2\cdot CMe_2\cdot CH_2\cdot CHBrMe,HBr$, which, after recrystallisation from benzene, melts at 160—161°; it yields a *picrate* crystallising from water in yellow scales melting at 157°, the corresponding *hydrochloride of γ-chlorhexylamine*, when recrystallised from dilute alcohol, melts at 157°; *μ-phenyl-α-dimethyl-γ-methylpentoxazoline*,  $N\leqslant\begin{array}{l}CMe_2\cdot CH_2\\ CPh——O\end{array}>CHMe$, prepared from γ-bromhexylamine hydrobromide and benzoic chloride, forms snow-white scales melting at 32°, and yields a yellow *picrate* melting at 162·5—164°, and a red *platinochloride.* By the action of thiobenzamide on the hydrobromide, *μ-phenyl-α-dimethyl-γ-methylpenthiazoline*,


$$N\leqslant\begin{array}{l}CMe_2\cdot CH_2\\ CPh——S\end{array}>CHMe,$$

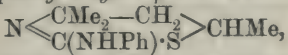
is produced; this forms rhombic plates melting at 34°, and gives a *picrate* crystallising from alcohol in yellow, rhombic prisms melting at 152°, also a *platinochloride* decomposing at 223°; *μ-mercapto-α-dimethyl-γ-methylpenthiazoline*,  $N\leqslant\begin{array}{l}CMe_2\cdot CH_2\\ C(SH)—S\end{array}>CHMe$, is formed when the hydrobromide reacts with carbon bisulphide in the presence of sodium hydroxide; it crystallises from methylic alcohol in thick prisms melting at 180°. Its *methylic* salt, which is obtained as a strongly refractive, colourless oil of peculiar odour when the mercaptan is treated with sodium methoxide and methylic iodide in methylic alcohol solution, boils at 240° (761·5 mm.); the *picrate* of the methylic salt melts at 131° and the *platinochloride* decomposes at 190°.

Amidohexanesulphonic acid, $\mathrm{NH_2{\cdot}CMe_2{\cdot}CH_2{\cdot}CHMe{\cdot}SO_3H}$, (2-methyl-2-amido-4-methyl-4-pentansulphonic acid) is formed by the oxidation of the above mercaptan, or, better still, its methylic salt, by means of chlorine; it does not melt below 310°.

Phenylhydroxyhexylthiocarbamide,

$$\mathrm{OH{\cdot}CHMe{\cdot}CH_2{\cdot}CMe_2{\cdot}NH{\cdot}CS{\cdot}NHPh},$$

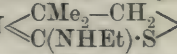
prepared from diacetonalkamine and phenylthiocarbimide, separates from hot alcohol in snow-white crystals melting at 163—164°; on treatment with concentrated hydrochloric acid in a closed tube at 100°, it is converted into *N-phenylhexylen-ψ-thiocarbamide*,



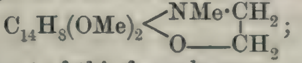
$$\mathrm{N}{<}\begin{array}{l}\mathrm{CMe_2{-}CH_2}\\ \mathrm{C(NHPh){\cdot}S}\end{array}{>}\mathrm{CHMe},$$

which separates from dilute alcohol in crystals melting at 147—148°, and gives a *platinochloride* decomposing at 202°. With ethylthiocarbimide, diacetonalkamine yields *hydroxyhexylthiocarbamide*,

$$\mathrm{OH{\cdot}CHMe{\cdot}CH_2{\cdot}CMe_2{,}NH{\cdot}CS{\cdot}NHEt},$$

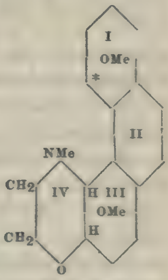
melting at 198·5°, and which with concentrated hydrochloric acid gives *N-ethylhexylene-ψ-thiocarbamide*,  $\mathrm{N}{<}\begin{array}{l}\mathrm{CMe_2{-}CH_2}\\ \mathrm{C(NHEt){\cdot}S}\end{array}{>}\mathrm{CHMe}$, which, however, was not obtained in a crystalline condition; the *picrate* melts at 156—157°, and the *platinochloride* decomposes at 190—191°. J. F. T.

Thebaine. By MARTIN FREUND (*Ber.*, 1897, **30**, 1357—1393).—It will be convenient, for purposes of explanation, to give at once the formula that the author adopts for thebaine as a result of his investigations. The two methoxyl groups are in rings I and III respectively; that in I must be in one of the two positions indicated by an asterisk; that in III is very possibly at the lowest angle of the hexagon. In this abstract, the formula just given will be abbreviated to



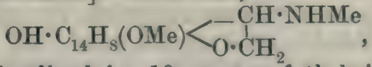
$$\mathrm{C_{14}H_8(OMe)_2}{<}\begin{array}{l}\mathrm{NMe{\cdot}CH_2}\\ \qquad\quad\mid\\ \mathrm{O{-\!\!-}CH_2}\end{array};$$

the left-hand part of this formula, corresponding with the right-hand part of the larger one, is to be regarded as a dihydrophenanthrene nucleus.



Thebaine.

[With HUGO MICHAELS].—Thebenine,

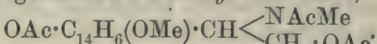


$$\mathrm{OH{\cdot}C_{14}H_8(OMe)}{<}\begin{array}{l}\mathrm{{-}CH{\cdot}NHMe}\\ \qquad\mid\\ \mathrm{O{\cdot}CH_2}\end{array},$$

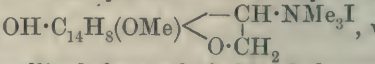
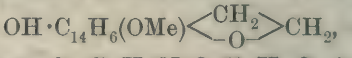
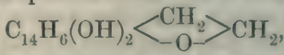
is best obtained by dissolving 10 grams of thebaine at a time in a 100 c.c. of nearly boiling hydrochloric acid of sp. gr. 1·07, boiling for 1½—2 minutes, cooling in ice and water, and recrystallising the hydrochloride, which separates, at first as a syrup, from hot water. The hydrochloride, with $3H_2O$, melts at 235°; the oxalate,

$$\mathrm{C_{18}H_{19}NO_3{,}C_2H_2O_4 + H_2O},$$

at 275—276° when heated quickly; the sulphate, $(C_{18}H_{19}NO_3)_2,H_2SO_4 + H_2O$, melts at 209—210°, and does not lose its water of crystallisation at 130—140°. Boiling with acetic anhydride converts thebenine into a substance which melts at 72—80° when crystallised from water, but when crystallised from absolute alcohol at 160—161°; it contains one methoxyl group, and cannot be reconverted by hydrolysis into thebenine; it is regarded as a *triacetyl* derivative,



$$OAc\cdot C_{14}H_6(OMe)\cdot CH<\begin{smallmatrix}NAcMe\\ CH_2\cdot OAc\end{smallmatrix}.$$

Thebenine, when boiled with phenylthiocarbimide in alcoholic solution, yields an amorphous *thiocarbamide*, $NHPh\cdot CS\cdot NC_{18}H_{18}O_3$, melting and decomposing at 85°. It also yields, with methylic iodide, thebeninemethinemethyliodide,  $OH\cdot C_{14}H_8(OMe)<\begin{smallmatrix}-CH\cdot NMe_3I\\ |\\ O\cdot CH_2\end{smallmatrix}$, which melts at 206—208° when crystallised from alcohol, and decomposes into thebenol and trimethylamine when boiled with 30 per cent. aqueous soda; with ethylic iodide, thebenine yields an analogous compound, which decomposes into thebenol and methyldiethylamine. These reactions show that thebenine is a secondary base; were it a tertiary base, the amine obtained in the last case would have been dimethylethylamine. *Thebenol*,  $OH\cdot C_{14}H_6(OMe)<\begin{smallmatrix}CH_2\\ -O-\end{smallmatrix}>CH_2$, melts at 186—188°; its *sodium hydrogen* salt, $C_{17}H_{13}NaO_3,C_{17}H_{14}O_3$, is completely melted at 210—212°. From 100 grams of thebaine, 60 of thebenine hydrochloride, 67 of the methinemethyliodide, and 33·5 of thebenol can be obtained. Thebenol gives an *acetyl* derivative melting at 102—103°, and a *methyl* derivative, melting at 133—134°. When boiled down with 30 per cent. aqueous potash until the water is nearly all driven off, it yields *northebenol*,  $C_{14}H_6(OH)_2<\begin{smallmatrix}CH_2\\ -O-\end{smallmatrix}>CH_2$, which melts at 202—203°; both this and thebenol itself, when boiled with strong hydriodic acid, give an *iodhydrin*, $C_{14}H_6(OH)_3\cdot CH_2\cdot CH_2I$, which is completely decomposed at 270°. Thebenol, further, is reduced to pyrene when it is distilled with zinc dust in a current of hydrogen, or when it is heated with strong hydriodic acid and phosphorus for 3—4 hours in a sealed tube at 220°.

[With ERNST GÖBEL].—When thebaine is boiled with acetic anhydride and anhydrous sodium acetate, it yields acetylthebaol and methylhydroxyethylamine, $NHMe\cdot CH_2\cdot CH_2\cdot OH$, the aurochloride of which melts at 145—-147° (Knorr's substance, Abstr., 1889, 1218, was probably impure). The methiodide, under similar circumstances, yields acetylthebaol and dimethylhydroxyethylamine, the yellow aurochloride of which, $CH_{11}NO,HAuCl_4$, melts at 195°; but when it is boiled with aqueous potash, the amine evolved is *tetramethylethylenediamine*, $NMe_2\cdot CH_2\cdot CH_2\cdot NMe_2$, for it is identical with the product formed when dimethylamine (2 mols.) is heated with ethylenic bromide (1 mol.) for 3 hours at 100° in a sealed tube; the *hydrochloride*, with 2HCl of this base, decomposes at 300°; the *aurochloride*, with $2HAuCl_4$, at 205°; the *platinochloride*, with H_2PtCl_6, at 252°. *Acetylthebaol*, $C_{18}H_{16}O_4$, melts at 118—120°; with bromine in chloroform solution, it gives a *dibromo*-substitution derivative, $C_{18}H_{14}Br_2O_4$, melting at 179°; and, when hydrolysed with alcoholic sodium ethoxide, it yields *thebaol*, $C_{14}H_7(OMe)_2 \cdot OH$, which melts at 94°, and gives phenanthrene when distilled with zinc-dust in a current of hydrogen. Acetylthebaol is oxidised by chromic acid in acetic acid solution or by permanganate in cold dilute sulphuric acid to yellow *acetylthebaolquinone*, $C_{18}H_{14}O_6$, which melts at 203°, gives a red *bromo*-substitution derivative, $C_{18}H_{13}BrO_6$, melting at 310°, and is hydrolysed by alcoholic sodium ethoxide to yellow *thebaolquinone*, $C_{14}H_5O_2(OMe)_2 \cdot OH$, which melts at 233°. These two quinones are hydroxydimethoxyphenanthrenequinones; they both condense with 3 : 4-tolylenediamine yielding dye-stuffs which are yellow in colour, but are turned purple-red by strong hydrochloric acid, and form a blue solution in strong sulphuric acid, and melt at 201—203° in the case of the acetyl derivative, at 192° in the other case. Thebaolquinone is oxidised by permanganate in the presence of cold dilute sulphuric acid to 1 : 2 : 3-methoxyphthalic acid, which melts at 138—144°, forming the anhydride, which then melts at 93—94° (Jacobsen, Abstr., 1883, 1124, gives 160° and 187°); this shows that the methoxyl group in the I ring of thebaine must be in one of the ortho-positions relatively to the II ring. When acetylthebaolquinone is oxidised with chromic acid in acetic acid solution, a smell of vanillin is always noticed when the product is being worked up; this makes it not unlikely that the methyl group in the III ring of thebaine may be in the ortho position relatively to the O atom of the IV ring. C. F. B.

Leuponic and Hexahydrocinchomeronic Acids. By Wilhelm Koenigs (*Ber.*, 1897, **30**, 1326—1332).—Hexahydrocinchomeronic acid, obtained by reducing monethylic cinchomeronate with sodium in boiling alcoholic solution (Abstr., 1896, i, 698), and melting at 237—238°, appears to be a mixture of the *cis*- and *trans*-modifications; heating with potassium hydroxide and a little water for 5—6 hours at 190—200° apparently converts it entirely into the more stable modification, for the acid, when regenerated after this treatment, melts and decomposes at 268—270° (or at 275° when heated quickly). It now crystallises in monoclinic tables, which were submitted to measurement; the very soluble *hydrochloride* and *hydrobromide* melt and decompose at 240—242° and 220—222° respectively, the *aurochloride* at 205°; the acid is optically inactive. Leuponic acid was obtained from the oxidation products of cinchonine (Skraup, this vol., i, 99); it is feebly dextrorotatory, and forms a colourless *nitrosamine* which melts and decomposes at 167—168°. When heated with potash and a little water, it is transformed into an acid identical in all respects with that described above. Leuponic acid must, then, be the unstable modification of cinchomeronic acid, and hence it must contain a pyridine ring. The author assigns to meroquinenine, cincholeuponic acid, and leuponic acid the constitution of hexahydropyridine (piperidine) derivatives, the 3 : 4 positions being occupied, in the respective cases, by the groups $CH{:}CH_2$ and $CH_2 \cdot COOH$, COOH and $CH_2 \cdot COOH$, and COOH and COOH. C. F. B.

Some Derivatives of Meroquinenine and Cincholeuponic Acid. By Wilhelm Koenigs (*Ber.*, 1897, **30**, 1332—1337).—Cincholeuponic acid, when heated for 5 to 6 hours with potash and a little water (compare preceding abstract) is converted into an isomeric *acid*, $C_8H_{11}NO_4$, which is lævorotatory and melts and decomposes at about 246°; the *hydrochloride* and *nitrosamine* melt and decompose at 197° and 173—175° respectively.

1-*Ethylcincholeuponic acid*, $C_{10}H_{17}NO_4$, is obtained by treating diethylic cincholeuponate with ethylic iodide, and hydrolysing the product with dilute hydrochloric acid; it melts and decomposes at 214—215°. When boiled with acetic anhydride, it yields two isomeric substances, $C_{10}H_{15}NO_3$; the α-compound, formed in larger amount, melts at 194°, the β-isomeride at 105°. Both have the character of *anhydro-acids*; with silver carbonate, they yield *silver* salts, $C_{10}H_{14}NO_3Ag$, from which the anhydro-acids can be regenerated. The α-compound, when boiled with barium hydroxide, yields a *barium* salt, $(C_{10}H_{16}NO_4)_2Ba$, and the *acid* that can be liberated from this melts and decomposes at 228° (its *hydrochloride* at 180°) and is isomeric with the ethylcincholeuponic acid described above; when boiled with acetic anhydride, however, it gives the same mixture of α- and β-anhydro-acids.

When meroquinenine is heated with arsenic acid for 2 to 3 hours at 180—190°, hardly any oxidation takes place, but it is converted into a substance, $C_9H_{17}NO_3 + 2H_2O$, which melts at about 220° when anhydrous, its *hydrochloride* at 254—255°; to this substance is assigned provisionally the constitution of a *lactone*, the corresponding acid being the hexahydropyridine derivative, $[CH(OH)\cdot CH_3 : CH_2\cdot COOH = 3 : 4]$; an isomeric substance, the *hydrochloride* of which melts at 223—224°, is also formed in the reaction.

The *ethylic* salt of 1-*ethylmeroquinenine*, $C_{13}H_{23}NO_2$, is formed when the ethylic salt of meroquinenine is treated with ethylic iodide; its *hydrochloride* and *hydrobromide* melt at 165° and about 215° respectively. When the latter is brominated in chloroform solution, the compound $C_{13}H_{23}Br_2NO_2,HBr$, melting at about 182°, is formed, and this is converted by prolonged boiling with very dilute hydrobromic acid into a substance, $C_{11}H_{18}BrNO_2,HBr$, which melts at 218—220°.

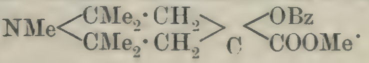
C. F. B.

Constitution of Emetine. By HERMANN KUNZ-KRAUSE (*Chem. Centr.*, 1896, ii, 894; from *Schweiz. Woch. Pharm.*, 34, 358. Compare Abstr., 1895, i, 118).—The author still regards the emetine he used as pure, in spite of Paul and Cownley's attempts to prove it a mixture of cephaeline and emetine. It has the formula $C_{30}H_{40}N_2O_5$, and contains four methoxy-groups. On oxidation with alkaline permanganate, it yields a yellow, amorphous substance, which, on further oxidation with nitric acid, forms a substance having a strong odour of sumbul root, and two acids containing nitrogen; the one gives a red coloration with ferrous sulphate, but the other does not react with it, and hence cannot be a 2-pyridinecarboxylic or 2′-quinolinecarboxylic acid. The latter acid, when heated with potassium, gives carbylamine, hence the author concludes that it, like emetine itself, does not contain a side chain united to nitrogen.

E. W. W.

Constitution of Pilocarpine. By PETER KUNDSEN (*Chem. Centr.*, 1896, ii, 708; from *Ber deutsch. Pharm. Ges.*, 6, 164—172).—According to Hardy and Calmel, pilocarpine is a derivative of a β-substituted pyridine, since when oxidised it yields first pyridinetartronic acid and then nicotinic acid, and contains also a pentavalent nitrogen atom, since it may be synthesised from trimethylamine and pyridinelactic acid. The author does not place absolute confidence in these results, since no analyses are quoted, and only very insufficient details of the yields obtained in the various decompositions. He describes his own attempts to prepare pyridinelactic acid, to synthesise picolinelactic acid from aldehydecolidine (2 : 3-dimethylpyridine), and to obtain higher homologues of pilocarpine. E. W. W.

Eucaine. By GEORG MERLING (*Chem. Centr.*, 1896, ii, 709; from *Ber. deutsch. Pharm. Ges.*, 6, 173—176).—Amygdalylmethyltriacetonealkamine, prepared from methyltriacetonealkamine, is, like tropine, a derivative of 4-hydroxymethylpiperidine, and to this the similarity of the physiological action of atropine, homatropine, and this alkamine is to be ascribed. Cocaine is a derivative of 4-hydroxypiperidinecarboxylic acid, and is closely related to atropine. The author describes experiments made to introduce benzoyl and methyl groups into the synthetically prepared 4-hydroxypiperidinecarboxylic acid, with a view to the preparation of anæsthetics which act locally. The synthesis of 3-hydroxypiperidinecarboxylic acid whose composition is analogous to that of ecgonine is also described. Eucaine, which is also obtained, and whose chloride is used in commerce as a substitute for cocaine, has the formula



$\mathrm{NMe}<\begin{array}{l}\mathrm{CMe_2\cdot CH_2}\\ \mathrm{CMe_2\cdot CH_2}\end{array}>\mathrm{C}<\begin{array}{l}\mathrm{OBz}\\ \mathrm{COOMe}\end{array}$. E. W. W.

Iodine Reaction of Chitin. By ENOCH ZANDER (*Pflüger's Archiv*, 1897, 66, 545—573).—For the iodine reaction of carbohydrates, water and some assisting substance must be present. The effect of various concentrated reagents on the colour reaction may be thus tabulated:

	Glycogen.	Soluble Starch.	Rice Starch.	Cellulose according to amount of iodine used.
Water	Weaker	Weaker	Weaker	Pale yellow to dark brown.
Zinc chloride, 70°/₀	Disappears	Blue	Blue	
Zinc sulphate	Deeper	Violet	Brown	Colourless to dark violet.
Alum		Blue		—
Sodium acetate	Becomes violet	Red		—
Sodium chloride	Deeper	Deep blue.		Yellow to dark brown.
Ammonium chloride		Blue		Yellow to dark brown.

In accordance with the relationship held to exist between chitin and carbohydrates, it is found that the iodine reaction it gives is almost identical with that given by glycogen. W. D. H.

Properties of Albumoses. By Fr. Kutscher (*Zeit. physiol. Chem.*, 1897, 23, 115—120).—The research relates principally to deutero-albumose prepared from Witte's peptone. Its reactions are in the main those which have previously been described; some small points of difference in detail are noted. The principal new fact observed is that a solution of deutero-albumose, or of proto-albumose, or of Witte's peptone, causes a precipitate of serum-globulin, vitellin, myosin, or muscle-syntonin, when it is added to a solution of these substances in sodium carbonate. These products of digestion also precipitate nuclein from a neutral solution of nucleic acid in sodium carbonate Egg-albumin or serum-albumin is not precipitated. W. D. H.

Organic Chemistry.

Acetylene Solutions and their Explosive Properties. By Iarcellin P. E. Berthelot and Paul Vieille (*Compt. rend.*, 1897, 24, 988—996, and 996—1000).—The authors have measured the ressures exerted at various temperatures between 3° and 75° by soluions of acetylene in acetone, the latter being saturated with the gas t 15° and under initial absolute pressures of about 7 kilos., 12 kilos., nd 20·5 kilos. respectively. The volume of the gas dissolved per litre f acetone and per kilogram of absolute pressure varied in the three eries from 23 to 24·6 volumes, and the volume dissolved increases roportionally with the pressure, as Claude and Hess have already bserved. It is noteworthy that the pressures can be represented by Regnault's formula for the pressures of the saturated vapours of a arge number of compounds, $\log F = a + b\alpha^t$, the constants for solutions of cetylene in acetone being $a = 5·1134$, $b = 1·5318$, and $\log \alpha = \bar{1}.99696$, being very nearly the same as, and $\log \alpha$ being identical with, the orresponding value as given by Regnault for acetone alone. In all he series of experiments, the vapour pressure of the acetone was a very mall proportion of the total pressure observed. It is very remarkable hat the pressure of the gas in solution should follow the same general aw as the pressures of the saturated vapours of homogeneous liquids, nd that the value of $\log \alpha$ should be $\bar{1}.997$, which Regnault regarded s a constant common to all compounds.

Experiments were made to ascertain the effect (1) of a discharge of nercury fulminate, and (2) of an incandescent wire, on the solutions of cetylene in acetone. When the liquid has been saturated with the as under an initial pressure not exceeding 13 kilos. at 15°, the exploion of the fulminate produces neither ignition nor explosion of the cetylene, and in this respect the solution of the gas resembles solutions f nitroglycerol in methylic alcohol. It will be seen later, however, hat this ceases to be true under higher pressures.

When the acetone has been saturated with acetylene under a pressure not exceeding 10 kilos., the effect of an incandescent wire on the gas bove the liquid is to cause the decomposition of the gas above the iquid, the pressure developed being the same as when pure acetylene s decomposed under the same pressure, but the decomposition does not extend to the gas that is dissolved in the liquid. When the wire s in the liquid, some of the dissolved gas is expelled by the rise of emperature, and this causes an elevation of pressure, but the decompoition is limited to the gas liberated from the liquid.

As the proportion of acetylene to acetone is increased by saturating he liquid with the gas under a higher pressure, the extent to which lecomposition proceeds under the conditions specified is increased, and when saturation has taken place under pressures exceeding 20 kilos., an ncandescent wire, either in the liquid or in the gas above it, brings bout the decomposition of the whole of the acetylene with the producion of pressures of several thousand atmospheres. At the same time, the propagation of the explosive wave takes place with extreme slowness, and the decomposition in one case required 0·387 of a second. The development of pressure is at first very rapid, and afterwards much slower. The whole of the acetone is decomposed at the same time as the acetylene, the products being carbon, hydrogen, carbonic oxide, and carbonic anhydride.

Experiments made with large cylinders such as are used for holding compressed gases gave results similar to those obtained with the experimental tubes. No practicable receiver is capable of resisting the pressure developed by the complete decomposition of the acetylene and acetone.

In order to be within the limits of safety, it is important that the acetone should be saturated at pressures not exceeding 6 or 8 kilos., and that the cylinder be not exposed to such a rise of temperature as will bring the internal pressure up to a dangerous point. It is clear, however, that acetylene, when dissolved in a liquid like acetone, is much less dangerous than when pure, and a much larger quantity of the gas can be contained in a cylinder of a given size and yet remain within the limits of safety, when in the form of a solution, than when in the gaseous state. It is necessary, however, that the cylinders should be as strong as those generally used for containing liquefied carbonic anhydride. If from any cause the internal pressure approaches 20 kilos., the conditions become very dangerous.

An examination of the thermochemistry of the changes involved shows that the heat developed by the decomposition of the acetylene is not sufficient to compensate for the heat absorbed by the volatilisation and decomposition of the acetone, and at the same time to raise the temperature of all the substances concerned up to the point at which acetylene decomposes, except when the proportion of acetylene to acetone exceeds a certain limit, and this limit can only be reached under pressures which approach 20 kilos. At the same time, it is noteworthy that the decomposition of the acetone, notwithstanding the absorption of heat that it involves, greatly increases the pressure inside the vessel. The decomposition of the acetylene, resulting in the development of a large quantity of heat and a very high pressure, produces an instantaneous internal heating of the system similar to that produced by sudden compression, which, as Berthelot has shown, is capable of decomposing nitrous oxide.

The reaction described affords another example of the fact that a high pressure not only does not prevent the occurrence of exothermic reactions, but on the contrary assists them by increasing the velocity and lowering the limit of inflammability. C. H. B.

Propagation of Decomposition in Pure Acetylene Solutions. By Marcellin P. E. Berthelot and Paul Vieille (*Compt. rend.*, 1897, **124**, 1000—1004).—Experiments were made with a view to ascertain, if possible, the exact conditions under which decomposition is not propagated through a mass of acetylene, whether initiated by an incandescent wire or by the explosion of a small quantity of fulminate. The former corresponds with local heating such as may be caused by friction or by the action of a small quantity of water on a large mass of carbide, the latter corresponds with the explosion of small quantities of metallic acetylides such as might be formed by the contact of the acetylene with copper or its alloys in presence of ammonia or certain salts. Some experiments were made in vessels of from 4 to 25 litres capacity, with a diameter equal to their height; others were made in tubes 22 mm. in diameter and 3 metres long.

In the large vessels, with an incandescent wire, no inflammation of the gas took place under pressures not exceeding 520 mm. above normal pressure; there was inflammation in one case out of five with 610 mm. above normal, and in four cases out of seven with 700 above normal.

With mercury fulminate, there was no propagation of the decomposition when the pressure did not exceed 170 mm. above normal, but with 240 mm. above normal there was occasional propagation, and with higher pressures it became more frequent. These results are not materially influenced by the capacity of the vessel.

The experiments show that it is not possible to fix a limit below which propagation certainly will not take place and above which it certainly will take place. The probability of an explosion increases continuously with the pressure. For practical purposes, it would seem that there is very little danger of explosion by ignition when the pressure is not more than 520 mm. above normal, and of explosion by detonation when the pressure is not more than 170 mm. above normal.

In the experiments with the tube, there was no propagation of decomposition even with 0·1 gram of fulminate when the pressure did not exceed 760 mm. above atmospheric pressure. C. H. B.

Action of Acetylene on Silver Nitrate. By GEORGES ARTH (*Compt. rend.*, 1897, **124**, 1534—1536).—Silver acetylide is variously described as yellow and white. In reality, the precipitate formed on passing the gas through an ammoniacal solution of silver nitrate is at first yellow, but subsequently becomes colourless, even when excess of the hydrocarbon is employed. The compound $C_2Ag_2,AgNO_3$ (Keiser, Abstr., 1892, 1416) becomes deep yellow when treated with ammonia, but soon becomes colourless.

Silver acetylide, C_2Ag_2, is always produced when excess of acetylene is passed through an ammoniacal solution of silver nitrate, but the compound $C_2Ag_2,AgNO_3$ is formed in ordinary aqueous solutions, and is pure only when these are sufficiently concentrated. An N/2 solution of silver nitrate yields a colourless product, and the precipitate does not begin to be yellow until the dilution reaches N/24; the quantity of nitric acid set free increases with the dilution. It therefore appears that the initial action of acetylene on a neutral solution of silver nitrate gives rise to the compound $C_2Ag_2,AgNO_3$, which is converted into a yellow, intermediate compound of unknown composition, capable of existence in presence of ammonia, this substance ultimately yielding silver acetylide.

Silver acetylide and the compound $C_2Ag_2,AgNO_3$ dissolve readily in a solution of potassium cyanide, acetylene being regenerated.

M. O. F.

Preparation of Ether. By L. LÉON A. PRUNIER (*Compt. rend.*, 1897, **124**, 1239—1242).—The formation of sulphonic derivatives during the preparation of ether (next abstract) indicates that the generally accepted explanation of the process is insufficient. It may be assumed that ethylic hydrogen sulphate, in contact with alcohol, forms diethylic sulphate, and the latter in contact with more alcohol yields ether, ethylic hydrogen sulphate being regenerated. Experiment shows that both ethylic hydrogen sulphate and diethylic sulphate yield sulphonic derivatives when heated between 100° and 140°, and it is noteworthy that the liberation of sulphurous anhydride and of ethylene in the action of sulphuric acid on alcohol begins at 130—140°. It may be assumed that, at 130—140°, ethylic hydrogen sulphate splits up into alcohol and sulphuric anhydride, and the latter, in presence of alcohol, forms isethionic acid, and subsequently its ethylic salt, $OH\cdot C_2H_4\cdot SO_2\cdot OEt$. The ethylic isethionate, in presence of alcohol, yields ether and isethionic acid, which is again converted into the ethylic salt, and so the cycle proceeds. At 140°, ethylic isethionate itself splits up into alcohol and sulphurous anhydride.

The behaviour of isethionic acid may be regarded as typical of that of other compounds of the same class. Ethylsulphonic acid, for example, by which it is most probably accompanied, would behave in a similar way. This view of the mode of production of ether is supported by the known process in which ether is obtained by the action of alcohol on benzenesulphonic acid, with intermediate formation of ethylic benzenesulphonate.

The limitation of the action is, in a large measure, due to the gradual removal of sulphuric acid from the sphere of activity, either in the form of sulphurous anhydride or by dilution by the water which is one of the products. C. H. B.

[Formation of Sulphonic Derivatives in the] Preparation of Ether. By L. Léon A. Prunier (*Compt. rend.*, 1897, **124**, 1028—1029). —Sulphonic derivatives exist in notable quantities in ordinary ether, from which they are readily removed by washing, but they exist in still larger quantities in the residues from the preparation of ether, and also in the liquids used for purifying it. They are produced by the action of moderately dilute sulphuric acid on ethylic hydrogen sulphate at 140°, and in the manufacture of ether they are produced in largest quantity when the temperature exceeds 140°, and especially when concentrated sulphuric acid is employed.

If the process is stopped when the liquid begins to turn black (165—175°), which is the point at which the liberation of ethylene begins, the liquid contains a large quantity of the sulphonic derivatives, which, after removal of sulphurous anhydride and decomposition of the ethylic hydrogen sulphate by boiling with water, can be separated in the form of barium salts in the usual way. C. H. B.

Action of Potash on Formaldehyde. By Marcel Delépine (*Compt. rend.*, 1897, **124**, 1454—1457).—When a concentrated solution of formaldehyde is diluted with water, development of heat occurs, but this phenomenon is followed by an absorption, which gradually reduces the temperature of the solution below the original point. Although the initial change may be followed quantitatively, and is found to be proportional in intensity to the degree of dilution, the absorption of heat is too gradual to admit of calorimetric determination.

Addition of a dilute or concentrated solution of formaldehyde to aqueous potash, on the other hand, causes immediate rise of temperature, unattended, however, with a secondary change. The numerical results, comformably with those obtained by Berthelot from acetaldehyde, show that the heat generated diminishes with dilution, but is augmented by excess of potash or of aldehyde, the latter displaying a more energetic influence than the alkali; also, that the energy of 3, 15, and 30 per cent. solutions of formaldehyde is the same, and that the energy regained during the heat absorption is equal to the heat lost on dilution.

Tollens and Grassmann observed that the freezing point of a freshly diluted formaldehyde solution is depressed to an increasing degree as time goes on, showing that such a solution does not attain a condition of equilibrium until a considerable period has elapsed. M. O. F.

Trioxymethylene and Paraformaldehyde. By Marcel Delépine (*Compt. rend.*, 1897, **124**, 1525—1528).—Determinations carried out with the calorimetric bomb gave the heat of combustion per gram-molecule (CH_2O), at constant pressure and volume, 122·9 Cal., the heat of formation of trioxymethylene, $C + H_2 + O = +40 \cdot 4$ Cal. If anhydrous trioxymethylene is boiled with water for many hours, it does not dissolve, it being necessary to heat the substances in sealed tubes at 130°; the aldehyde having the same heat of formation as trioxymethylene, its production from the latter is isothermic, but the formation of formic acid, methylic alcohol, and carbonic anhydride is decidedly exothermic.

A specimen of paraformaldehyde having the composition $(CH_2O)_8,H_2O$, gave the heat of combustion per gram-molecule (CH_2O), at constant pressure and volume, 120·8 Cal., whence the heat of formation amounts to +42·5 Cal. Paraformaldehyde probably represents one of the terms of the dehydration series, $nCH_2(OH)_2 = (CH_2O)n,H_2O + (n-1)H_2O$, of which the fundamental, $CH_2(OH)_2$, and the first terms are dehydrated on concentration, the products, which are less readily soluble, being deposited from the solution, but never dehydrated; complete dehydration only occurs under the influence of such an agent as sulphuric acid. Thus the transformation of paraformaldehyde into trioxymethylene absorbs 2·1 Cal. M. O. F.

Action of Water on Formaldehyde as Related to the Rôle of this Substance in Plants. By Marcel Delépine (*Bull. Soc. Chim.*, 1897, [iii], **15**, 997—1002).—When trioxymethylene is heated with an equal weight of water at 200°, it yields carbonic anhydride, methylic alcohol, formic acid, and a small quantity of carbonic oxide, the last-named product being due to the action of heat on the solution of formic acid; the same result is effected at 130—140°. During this change, the oxygen in the tube is completely absorbed, although a cold solution of formaldehyde does not absorb the gas.

The author discusses the bearing which these results have on the question of the *rôle* played by formaldehyde in plants. M. O. F.

Magnesium Malonate. By Gustave Massol (*Bull. Soc. Chim.*, 1896, [iii], **15**, 1103).—Magnesium oxide readily dissolves in solutions of malonic acid at the ordinary temperature. Concentrated solutions yield the *salt* $C_3H_2O_4Mg + 4{\cdot}5H_2O$ in the form of large, transparent, monoclinic crystals. It loses part of its water when heated at 100°, yielding the *hydrate* $C_3H_2O_4Mg + 2H_2O$, which is also obtained during the evaporation of the aqueous solution between 90° and 100°. The complete dehydration takes place at 200—210°, and the anhydrous salt, when dissolved in water, evolves a considerable amount of heat.

$$C_3H_4O_4 \text{ sol.} + MgO \text{ sol.} = C_3H_2O_4Mg \text{ sol.} + H_2O \text{ sol.} + 14{\cdot}88 \text{ Cal.}$$

J. J. S.

Zinc Malonate. By GUSTAVE MASSEL (*Bull. Soc. Chim.*, 1896, [iii], **15**, 1104).—*Zinc malonate* crystallises as $C_3H_2O_4Zn + 2{\cdot}5H_2O$ in large, brilliant, monoclinic crystals sparingly soluble in water, the heat of solution, (212 grams in 4 litres) = – 1·48 Cal. When finely powdered and heated to 100°, it yields the compound $C_3H_2O_4Zn + H_2O$, which dissolves in water evolving + 4·79 Cal. The whole of the water is driven off at 150°, and the heat of solution of the anhydrous salt is + 5·65 Cal. Decomposition begins at 160°, and at higher temperatures the salt burns, leaving a residue of zinc oxide.

$$C_3H_4O_4 \text{ sol.} + ZnO \text{ sol.} = C_3H_2O_4Zn \text{ sol.} + H_2O \text{ sol.} + 6{\cdot}66 \text{ Cal.}$$

J. J. S.

Racemic Transformation of Acid Ammonium Malate. By FRANK B. KENRICK (*Ber.*, 1897, **30**, 1749—1757).—If the monosymmetric crystals of the acid ammonium malate are heated, a change occurs at about 70—75° into rhombic crystals resembling those of the active salt. The author has carried out experiments for the purpose of ascertaining whether the racemic modification does actually decompose into its two active components in accordance with the equation

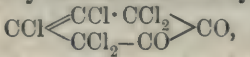
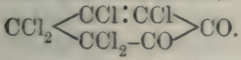
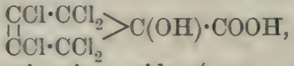
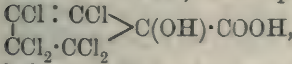
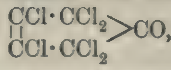
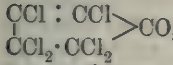
$$2C_4H_5O_5{\cdot}NH_4,H_2O = ({}^{\rightarrow}C_4H_5O_5{\cdot}NH_4 + {}^{\leftarrow})C_4H_5O_5{\cdot}NH_4 + 2H_2O.$$

The presence of excess of one of the active components has no influence on the temperature of change of the racemic modification. Above a temperature of 80°, the active malate crystallises from a solution of the inactive salt, and solubility experiments carried out below the temperature of change also indicate that the transformation of the racemic modification takes place in accordance with the above equation.

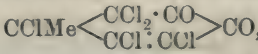
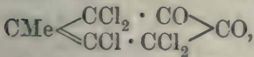
H. C.

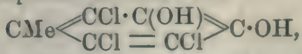
Preparation of Furfuran. By PAUL FREUNDLER (*Compt. rend.*, 1897, **124**, 1157—1159).—By the usual method of preparing furfuran, a very unsatisfactory yield of the substance is obtained. The author finds, however, that when pyromucic acid is heated in sealed tubes for 2 hours at 260—275°, a quantitative yield of furfuran is produced. When barium pyromucate is heated alone, the yield of furfurane exceeds the quantity of gases produced, but with increasing amounts of caustic soda, the yield of furfuran is diminished, and the quantity of gas, which is a mixture of carbonic oxide and a hydrocarbon, is very considerably increased. The *hydrocarbon*, C_3H_4, is ethylenic in character, and gives no precipitate with cuprous chloride or silver nitrate; the *tetrabromide*, $C_3H_4Br_4$, boils at 162° under a pressure of 20 mm., and rapidly undergoes decomposition at ordinary temperatures, yielding hydrogen bromide.

M. O. F.

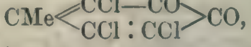
Action of Chlorine on Orthamidophenols and Orthodiamines. By E. C. THEODOR ZINCKE (*Annalen*, 1897, **296**, 135—158. Compare Abstr., 1895, i, 131).—The author's previous investigations have shown that chlorine converts orthamidophenol and catechol into the orthodiketo-chloride, $C_6Cl_6O_2$, which is also produced by the action of the halogen on orthophenylenediamine. Physical considerations now confirm the formula  $CCl<\begin{matrix}CCl\cdot CCl_2\\ CCl_2-CO\end{matrix}>CO$, originally proposed for this substance, but subsequently replaced by the expression  $CCl_2<\begin{matrix}CCl{:}CCl\\ CCl_2-CO\end{matrix}>CO$. Alkali converts the diketo-chloride into hexachloropentenehydroxycarboxylic acid,  $\begin{matrix}CCl\cdot CCl_2\\ \Vert\\ CCl\cdot CCl_2\end{matrix}>C(OH)\cdot COOH$, which melts at 111°, and passes into the isomeride (m. p. 186°),  $\begin{matrix}CCl : CCl\\ |\\ CCl_2\cdot CCl_2\end{matrix}>C(OH)\cdot COOH$, when heated. Both acids yield perchlorindone, C_9Cl_6O, when heated with water, whilst oxidation with chromic acid converts them into the isomeric ketones,  $\begin{matrix}CCl\cdot CCl_2\\ \Vert\\ CCl\cdot CCl_2\end{matrix}>CO$, and  $\begin{matrix}CCl : CCl\\ |\\ CCl_2\cdot CCl_2\end{matrix}>CO$, which melt at 28° and 92° respectively, and give rise to a mixture of the two substances when heated; alkali converts the ketones into the acids $CCl_2{:}C{:}CCl\cdot CCl_2\cdot COOH$ (m. p. 127°), and $CCl_2{:}CCl\cdot CCl{:}CCl\cdot COOH$ (m. p. 97—98°) respectively, both these compounds yielding ethylidenepropionic acid on reduction with sodium amalgam.

This summary of previous work is followed by a discussion of the results described in the following abstracts. M. O. F.

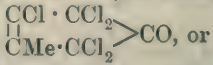
Action of Chlorine on Orthamidoparacresol and Orthotolylenediamine, 1-Methylpentachloro-3 : 4-diketo-R-hexene, and its Products of Change. By E. C. THEODOR ZINCKE, F. BERGMANN, and BRUNO FRANCKE (*Annalen*, 1897, **296**, 159—179).—1-*Methylpentachloro*-3 : 4-*diketo*-R-*hexene hydrate*,  $CClMe<\begin{matrix}CCl_2\cdot CO\\ CCl{:}CCl\end{matrix}>CO$, or  $CMe<\begin{matrix}CCl_2\cdot CO\\ CCl\cdot CCl_2\end{matrix}>CO$, is produced when orthotolylenediamine hydrochloride is suspended in glacial acetic and concentrated hydrochloric acids, and submitted to the action of a current of chlorine; 1 : 3 : 4-amidocresol may also be employed as the source of this substance. The compound is very readily soluble in glacial acetic acid, alcohol, and ether, but dissolves with difficulty in benzene, from which it separates in colourless, prismatic, highly-refractive crystals, containing $2H_2O$; it melts at 90°, and becomes anhydrous in the desiccator, yielding a red oil which solidifies on exposure to moist air.

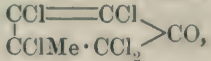
1 : 2 : 5 : 6-*Methyltrichlorocatechol*,  $CMe<\begin{matrix}CCl\cdot C(OH)\\ CCl=CCl\end{matrix}>C\cdot OH$, is obtained by reducing a solution of the foregoing compound in glacial acetic acid with stannous chloride, and precipitating with concentrated

hydrochloric acid; it crystallises from dilute acetic acid in white needles containing the solvent, and melts at 179—180°. Chlorination regenerates methylpentachlorodiketohexene hydrate. The *acetyl* derivative crystallises from glacial acetic acid in small, colourless plates, and melts at 161°.

1 : 2 : 5 : 6-*Methyltrichlororthobenzoquinone*,  $\mathrm{CMe}{<}\begin{matrix}\mathrm{CCl{-}CO}\\ \mathrm{CCl:CCl}\end{matrix}{>}\mathrm{CO}$, is formed when methyltrichlorocatechol, mixed with a small quantity of glacial acetic acid, is cautiously added to a mixture of glacial acetic and nitric (sp. gr. 1·4) acids in equal quantities. It dissolves with great readiness in all solvents excepting water, and forms a deep red powder melting at 103°. Reducing agents convert the quinone into the catechol derivative, and chlorine regenerates methylpentachlorodiketohexene hydrate. Caustic soda develops a deep blue coloration, which becomes yellowish, and sodium carbonate forms a brownish-red solution; hydrochloric acid precipitates methyltrichlorocatechol from both solutions.

Methylpentachloro-R-*pentenehydroxycarboxylic acid* [Me : OH = 1 : 3] is obtained by adding small quantities of finely-powdered methylpentachlorodiketohexene hydrate to a well cooled 10 per cent. solution of sodium carbonate, maintained at 0° by the addition of ice; the use of too much alkali is to be avoided, as the decomposition is apt to proceed farther. The solution is decanted from undissolved substance into concentrated hydrochloric acid in which ice is suspended, the precipitate being dissolved in an ice-cold solution of sodium acetate, and quickly filtered into concentrated hydrochloric acid. It crystallises from benzene in snow-white needles, and melts at 99·5°; it contains $1H_2O$, which is not eliminated in the desiccator. The *acetyl* derivative crystallises from benzene in small, white needles, and melts at 161°.

1-*Methylpentachloro*-3-*keto*-R-*pentene*,  $\begin{matrix}\mathrm{CCl\cdot CCl_2}\\ \|\\ \mathrm{CMe\cdot CCl_2}\end{matrix}{>}\mathrm{CO}$, or

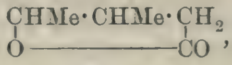
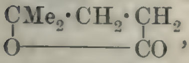


$$\begin{matrix}\mathrm{CCl{=\!=}CCl}\\ |\\ \mathrm{CClMe\cdot CCl_2}\end{matrix}{>}\mathrm{CO},$$

occurs in two modifications. The *a-ketone* is obtained by adding a 30 per cent. aqueous solution of chromic acid to a solution of the foregoing pentenehydroxycarboxylic acid dissolved in glacial acetic acid; it is a bright-yellow oil which has the sp. gr. = 1·608 at 15°, and boils at 160—165° under a pressure of 35 mm. Gaseous ammonia converts it into the *compound*, $NH_2\cdot C_5Cl_4MeO$, which crystallises from benzene in yellowish scales, and melts at 137°. The *β-ketone* is obtained by treating the original diketohexene derivative with excess of a hot solution of bleaching powder, and acidifying with hydrochloric acid; it forms large, monoclinic crystals, and melts at 92°. Gaseous ammonia has no action on the substance, which is converted by alcoholic ammonia into a dark, brownish-red oil; phenylhydrazine gives rise to the *compound* $C_5ClMe(N_2H_2Ph)_2O$, probably a pyrazolidone derivative, which crystallises from benzene in dark red needles or leaflets, and melts at 200°. *β-Methylpentachloro*-R-*pentene hydroxycyanide*, $OH\cdot C_5Cl_5Me\cdot CN$, is obtained by adding an alcoholic solution of potassium cyanide to a well-cooled solution of the ketone in absolute alcohol; it crystallises in thick needles, and melts, evolving gas, at 110°.

a-Methyltetrachlorobutinenecarboxylic acid, $CCl_2{:}C{:}CMe\cdot CCl_2\cdot COOH$, or $CCl_2{:}CMe\cdot CCl{:}CCl\cdot COOH$, is obtained by agitating the α-ketone with a well cooled 5 per cent. solution of caustic soda, and then acidifying with hydrochloric acid; it separates from dilute acetic acid in compact, colourless crystals, and melts at 146°. The *methylic* salt is a colourless oil having a feeble odour.

a-Methylbutylenecarboxylic acid, $CHMe{:}CMe\cdot CH_2\cdot COOH$, or $CMe_2{:}CH\cdot CH_2\cdot COOH$, is prepared by reducing the foregoing acid with sodium amalgam. It is a colourless oil, having the characteristic odour of fatty acids, and boils at 205—207°; its sp. gr. = 0·9884 at 17°. The *dibromide* crystallises from light petroleum in four-sided prisms, and melts at 104—105°.

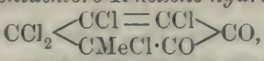
The *lactone* of methylhydroxyvaleric acid,  $\begin{array}{l}\mathrm{CHMe\cdot CHMe\cdot CH_2}\\ \mathrm{O}\text{———————}\mathrm{CO}\end{array}$, or  $\begin{array}{l}\mathrm{CMe_2\cdot CH_2\cdot CH_2}\\ \mathrm{O}\text{————}\mathrm{CO}\end{array}$, is obtained from the incompletely reduced chlorinated acid by the action of hot, dilute sulphuric acid; it boils at 85° under a pressure of 20 mm., and at 205·5° under atmospheric pressure.

When methylpentachloropentenehydroxycarboxylic acid is treated with water or sodium acetate, the indifferent *compound* $C_{10}Cl_6Me_2O_2$ is produced, and this substance also occurs as a bye-product in the preparation of the acid from the diketo-chloride; it separates from glacial acetic acid in small, colourless crystals, and melts at 182°, undergoing decomposition. Phosphorus pentachloride at 150° converts it into the *compound*, $C_{10}Cl_8Me_2O$, which crystallises from hot, glacial acetic acid, and melts at 245—247° in closed tubes, subliming below this temperature.

The *acid* $C_5Cl_2MeO_2\cdot COOH$ is another bye-product, and crystallises from dilute alcohol in short, slender needles, melting indefinitely at 218°; the *barium* salt crystallises from hot water in needles, and the *methylic* salt forms nacreous needles melting at 94·5°. M. O. F.

Action of Chlorine on Trichlororthodiamidotoluene, 1-Methyl-2:3-diketopentachloro-R-hexene and its Products of Change. By E. C. THEODOR ZINCKE and WILHELM PRENNTZELL (*Annalen*, 1897, **296**, 180—198).—With certain modifications, the authors have adopted Seelig's method for the preparation of 1:2:3:4:5:6-diamidotrichlorotoluene from 1:4:5:6-trichlorotoluene, and of the latter from the hydrocarbon.

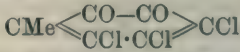
1-*Methyl*-2 : 3-*diketopentachloro*-R-*hexene hydrate*,



$$\mathrm{CCl_2}\!<\!\begin{array}{c}\mathrm{CCl=CCl}\\ \mathrm{CMeCl\cdot CO}\end{array}\!>\!\mathrm{CO},$$

is obtained by dissolving the diamine in glacial acetic and hydrochloric acids, saturating the liquid with hydrogen chloride, and then passing chlorine through the solution maintained at 5—10° until the dark colour changes to yellow; after some hours, the ammonium chloride is filtered off and the liquid evaporated at the ordinary temperature. The compound contains $2H_2O$, and melts at 86—88°.

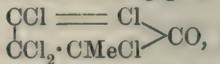
1 : 4 : 5 : 6-*Methyltrichlorocatechol*, $C_6MeCl_3(OH)_2$, is prepared from the foregoing keto-chloride by reducing the solution in glacial acetic acid with stannous chloride; it crystallises in long, white needles, becomes brown at 160°, and melts at 168°. Ferric chloride develops a violet coloration with the hot, aqueous solution. The *acetyl* derivative crystallises in colourless leaflets and melts at 165°.

1 : 4 : 5 : 6-*Methyltrichlororthobenzoquinone*,  $\mathrm{CMe}{<}\begin{matrix}\mathrm{CO{-}CO}\\ \mathrm{CCl{\cdot}CCl}\end{matrix}{>}\mathrm{CCl}$, is obtained by oxidising the catechol derivative with nitric acid; it dissolves with great readiness in organic solvents, and crystallises in dark red needles melting at 98°.

Methylpentachloro-R-*pentenehydroxycarboxylic acid*,

$C_5MeCl_5(OH){\cdot}COOH \quad [Me : OH = 1 : 2]$,

is produced when the finely powdered keto-chloride is added to a smaller quantity of 10 per cent. sodium carbonate solution than that required to dissolve it, the filtered liquid being immediately added to ice and hydrochloric acid. The oil which separates solidifies rapidly, and, when freshly crystallised, contains $1H_2O$ and melts at 90°; the lustrous, transparent scales become opaque in the desiccator, and the substance melts at 123°, evolving gas. The *acetyl* compound forms large, monoclinic prisms, and melts at 160°, evolving gas.

1-*Methylpentachloro-2-keto*-R-*pentene*,  $\begin{matrix}\mathrm{CCl} = \mathrm{Cl}\\ \mathrm{CCl_2{\cdot}CMeCl}\end{matrix}{>}\mathrm{CO}$, is obtained by the action of bleaching powder on the keto-chloride, and occurs in two modifications. The *a-ketone* is best prepared by oxidising the foregoing hydroxycarboxylic acid in glacial acetic acid with a 30 per cent. solution of chromic acid; it is a pale yellow oil of camphor-like odour, and is readily volatile in an atmosphere of steam. The substance boils at 155—156° under a pressure of 40—45 mm.; it has the sp. gr. = 1·610 at 19°, and the refractive index = 1·55127 at 21°. The *anilide* crystallises from alcohol in small, white needles, and melts at 195°; it becomes yellow when exposed to light, the colour being destroyed if the substance is kept in the dark. Alkali eliminates phenylcarbimide from the aniline derivative. Phenylhydrazine converts the α-ketone into the *compound* $C_{18}H_{15}N_4OCl$, which is probably a pyrazolidone derivative; it forms small, bright red needles, and melts at 202°. The *β-ketone* is obtained by agitating the keto-chloride with a solution of bleaching powder during several days, and acidifying the liquid with dilute hydrochloric acid; the mixture of ketones is distilled in a current of steam, and the liquid modification separated from the crystalline form by filtration. The β-ketone forms large, transparent crystals, and melts at 91°. Phenylhydrazine converts it into a compound melting at 197°, which is probably identical with the substance derived from the α-modification.

β-Methyltetrachlorobutinenecarboxylic acid,

$\mathrm{CMeCl{:}CCl{\cdot}CCl{:}CCl{\cdot}COOH}$,

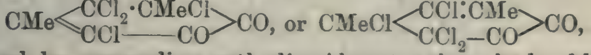
is prepared by adding the keto-chloride to a 10 per cent. solution of caustic soda with continual agitation, and filtering the liquid into hydrochloric acid; it crystallises from benzene in transparent prisms, and separates from dilute acetic acid in beautiful, white needles melting at 145°. The *sodium* and *potassium* salts dissolve readily in water, and the *ammonium* salt melts at 170°, evolving gas and becoming red; the *silver* salt crystallises from alcohol in small, white needles, the *barium* salt contains $5H_2O$, and the *methylic* salt is a colourless liquid.

β-Methylbutylenecarboxylic acid, $CH_2Me{\cdot}CH{:}CH{\cdot}CH_2{\cdot}COOH$, arises from the foregoing substance on reduction with sodium amalgam, and forms a colourless oil which boils at 120—123° under a pressure of 28 mm., and at 203—204° under atmospheric pressure. The *calcium* salt contains $3H_2O$, and the *silver* salt crystallises from water, but is in part reduced during the operation.

As in the case of α-methyltetrachlorobutinenecarboxylic acid (foregoing abstract), an indifferent *compound*, $C_{10}Cl_6Me_2O_2$, is produced when the keto-chloride is treated with caustic soda; it crystallises in small, colourless needles, and melts at 175°, evolving gas. The substance is also obtained by reducing the α-ketone with stannous chloride. M. O. F.

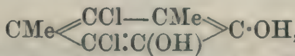
Action of Chlorine on Metamido-orthohydroxymetaxylene and Orthodiamidometaxylene, 1 : 3-Dimethyl-4 : 5-diketotetrachloro-R-hexene and its Products of Change.

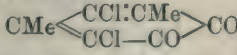
By E. C. Theodor Zincke and Bruno Francke (*Annalen*, 1897, **296**, 198—216).—1 : 3-*Dimethyl*-4 : 5-*diketotetrachloro*-R-*hexene hydrate*,

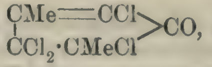


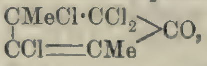
$$\mathrm{CMe}\left\langle\begin{matrix}\mathrm{CCl_2{\cdot}CMeCl}\\ \mathrm{CCl{-}{-}{-}CO}\end{matrix}\right\rangle\mathrm{CO},\ \text{or}\ \mathrm{CMeCl}\left\langle\begin{matrix}\mathrm{CCl{:}CMe}\\ \mathrm{CCl_2{-}CO}\end{matrix}\right\rangle\mathrm{CO},$$

is prepared by suspending orthodiamidometaxylene hydrochloride in glacial acetic and concentrated hydrochloric acids and saturating the liquid with chlorine, the colour of the solution finally becoming yellow; the ammonium chloride is removed by filtration, and the acetic acid allowed to evaporate at the ordinary temperature. The substance crystallises in colourless, monoclinic prisms containing $2H_2O$, and melts at 63°; at 64°, it becomes opaque and solidifies, but on cooling below 64°, it again becomes transparent and liquid; a second fusion occurs at about 130°, the substance beginning to boil at 196°, when it becomes brown. The *methoxide*, $OH{\cdot}C_6Me_2Cl_4O{\cdot}OMe$, is obtained by boiling a solution of the hydrate in methylic alcohol in a reflux apparatus, and pouring the concentrated liquid into water; it crystallises in transparent, monoclinic prisms, sinters at 100°, and melts at 118—120°. The hydrate may also be prepared from *metamido-orthohydroxymetaxylene*, which crystallises from alcohol in brownish, nacreous leaflets, and melts at 133—134°.

1 : 3-*Dimethyl*-2 : 6-*dichlorocatechol*,  $\mathrm{CMe}\left\langle\begin{matrix}\mathrm{CCl{-}CMe}\\ \mathrm{CCl{:}C(OH)}\end{matrix}\right\rangle\mathrm{C{\cdot}OH}$, is prepared by reducing the keto-chloride dissolved in glacial acetic acid with stannous chloride; it melts indefinitely at 149°, and sublimes if heated for some time at 110—120°. The *acetyl* derivative crystallises from glacial acetic acid, and melts at 161°.

1 : 3-*Dimethyl*-2 : 6-*dichlororthoquinone*,  $\mathrm{CMe}\left\langle\begin{matrix}\mathrm{CCl{:}CMe}\\ \mathrm{CCl{-}CO}\end{matrix}\right\rangle\mathrm{CO}$, is obtained by oxidising the catechol derivative with nitric acid; it forms a dark red, crystalline powder, and melts at 108°.

Dimethyltetrachloroketo-R-*pentene*,  $\left.\begin{array}{l}\mathrm{CMe{=}CCl}\\ \mathrm{CCl_2\cdot CMeCl}\end{array}\right>\mathrm{CO}$, or

 $\left.\begin{array}{l}\mathrm{CMeCl\cdot CCl_2}\\ \mathrm{CCl{=}CMe}\end{array}\right>\mathrm{CO}$,

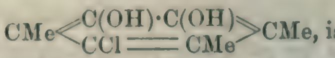
is obtained by the action of bleaching powder on the diketo-chloride, and occurs in two modifications. The *a-ketone* is liquid, and may be filtered from the solid modification; this crystallises from the oil after distillation in a current of steam, and boils at 135° under a pressure of 30 mm., but has not yet been obtained unmixed with the isomeride. The *β-ketone* separates from benzene in large, monoclinic crystals, and melts at 60°; it has a pungent odour suggestive of camphor, and is readily volatile at the ordinary temperature.

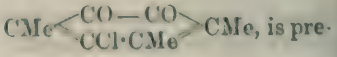
Dimethyltrichlorobutinenecarboxylic acid, $\mathrm{CMeCl\dot{:}CCl\cdot CMe\dot{:}CCl\cdot COOH}$, or $\mathrm{CCl_2\dot{:}CMe\cdot CCl\dot{:}CMe\cdot COOH}$, is prepared by dissolving the *a*-ketone in 10 per cent. caustic soda, and acidifying with hydrochloric acid; it crystallises from benzene in beautiful, rhombic plates, and melts at 112°.

Dimethylbutylenecarboxylic acid, $\mathrm{CH_2Me\cdot CH\dot{:}CHMe\cdot CH_2\cdot COOH}$, or $\mathrm{CMe_2\dot{:}CH\cdot CHMe\cdot COOH}$, is obtained from the foregoing compound by reduction with sodium amalgam; the *silver* salt is amorphous. When heated with water, it yields a *lactone*, which separates from light petroleum in monoclinic crystals and melts at 47—48°.

The indifferent *compound*, $\mathrm{C_{10}Cl_4Me_4O_2}$, is obtained by the action of caustic soda on the keto-chloride (compare foregoing abstracts); it separates from its solutions in large, monoclinic crystals, and melts at 173°. The substance is very indifferent towards alkalis, bases, and oxidising agents. The *acid*, $\mathrm{C_5ClMe_2O_2\cdot COOH}$, is another bye-product of the action of caustic soda on the keto-chloride, and crystallises from water or glacial acetic acid in small, white needles melting at 185°; the *silver* salt is a white, crystalline powder, and the *ammonium* salt forms white leaflets. The *methylic* salt crystallises from benzene and melts at 81·5°. M. O. F.

Action of Chlorine on Orthodiamido-ψ-cumene. By E. C. Theodor Zincke and Franz Hodes (*Annalen*, 1897, **296**, 216—219).—When chlorine acts on orthodiamido-ψ-cumene hydrochloride suspended in glacial acetic and hydrochloric acids, ammonium chloride separates, and the liquid becomes brown; no crystalline product has been obtained from the filtrate, but reduction of the oil obtained after evaporating the solvent gives rise to a derivative of catechol (compare foregoing abstracts).

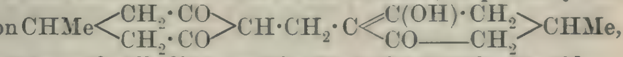
1 : 4 : 5 : 6-*Trimethylchlorocatechol*,  $\mathrm{CMe}<\begin{array}{l}\mathrm{C(OH)\cdot C(OH)}\\ \mathrm{CCl{=}CMe}\end{array}>\mathrm{CMe}$, is obtained by dissolving the oil in glacial acetic acid and reducing the solution with stannous chloride and hydrochloric acid; it crystallises from dilute alcohol or dilute hydrochloric acid, and melts at 131—132°. The *acetyl* derivative crystallises from glacial acetic acid in lustrous, colourless leaflets, and melts at 162—163°.

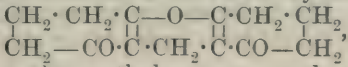
1 : 4 : 5 : 6-*Trimethylchlororthoquinone*,  $\mathrm{CMe}<\begin{array}{l}\mathrm{CO-CO}\\ \mathrm{CCl\cdot CMe}\end{array}>\mathrm{CMe}$, is pre-

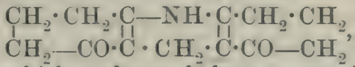
pared by oxidising the catechol derivative with nitric acid; it separates from benzene in small, dark-red crystals, and melts at 96—97°.

M. O. F.

Hydrogenation of Orcinol. By Daniel Vorländer and Fritz Kalkow (*Ber.*, 1897, **30**, 1801—1803).—When orcinol is heated with a solution of sodium hydrogen carbonate and sodium amalgam in a reflux apparatus while carbonic anhydride is passed through the liquid, metamethyldihydroresorcinol is produced (compare Knoevenagel, Abstr., 1896, i, 289). Methyldihydroresorcinol undergoes hydrolysis as in the case of dihydroresorcinol (this vol., i, 272); dimethyldihydroresorcinol (this vol., i, 276), however, resists the action of barium hydroxide in sealed tubes at 150—160°.

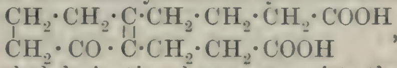
Methyldihydroresorcinol *dioxime* crystallises from boiling water in lustrous prisms, and melts at 155—157°. The formaldehyde *compound*, $C_{15}H_{20}O_4$, crystallises from hot alcohol in white needles, melts at 152°, and develops a brown coloration with ferric chloride; it probably has the constitution  $CHMe<\begin{matrix}CH_2\cdot CO\\CH_2\cdot CO\end{matrix}>CH\cdot CH_2\cdot C\ll\begin{matrix}C(OH)\cdot CH_2\\CO——CH_2\end{matrix}>CHMe$, as its behaviour towards alkalis resembles that of a monobasic acid.

Methylenebisdihydroresorcinol is converted by dehydrating agents into the *anhydride*,  $\begin{matrix}CH_2\cdot CH_2\cdot C—O—C\cdot CH_2\cdot CH_2\\ CH_2—CO\cdot C\cdot CH_2\cdot C\cdot CO—CH_2\end{matrix}$, which melts at 165°, and regenerates the methylene compound when heated with water in a sealed tube. Alcoholic ammonia converts methylenebisdihydroresorcinol into the acridine *compound*,



$$\begin{matrix}CH_2\cdot CH_2\cdot C—NH\cdot C\cdot CH_2\cdot CH_2\\ CH_2—CO\cdot C\cdot CH_2\cdot C\cdot CO—CH_2\end{matrix},$$

a yellow substance which melts and decomposes above 300°, and exhibits green fluorescence in solution; this derivative is also obtained by the action of ammonia on the foregoing anhydride, and yields acridine when distilled with zinc dust.

Boiling caustic alkali converts methylenebisdihydroresorcinol into the dibasic ketonic *acid*,  $\begin{matrix}CH_2\cdot CH_2\cdot C\cdot CH_2\cdot CH_2\cdot CH_2\cdot COOH\\ CH_2\cdot CO\cdot C\cdot CH_2\cdot CH_2\cdot COOH\end{matrix}$, which melts at 76°. The tetramethyl derivative, however, resists the action of alkali.

M. O. F.

Purification of Hydrocarbons from Thiophen, its Homologues, and other Impurities by means of Aluminium Chloride. Application to the Purification of Benzene and Toluene. By Albin Haller and Edmond Michel (*Bull. Soc. Chim.*, 1897, [iii], 15, 1065—1070. Compare Heusler, Abstr., 1895, i, 258).—Precipitation of thiophen with mercuric sulphate (Denigès, Abstr., 1895, ii, 372), is not applicable to purification of large quantities of benzene; aluminium chloride, however, may be used advantageously for this purpose.

The hydrocarbon is agitated with aluminium chloride, which develops a red coloration, and causes the deposition of a viscous liquid; after some time, the hydrocarbon is decanted from this product, and submitted to distillation, water, in any form, being carefully excluded.

The amount of aluminium chloride employed depends on the degree of purity of the benzene; a specimen which has already undergone treatment with sulphuric acid requires about 1 per cent., as much as 5 per cent. being used for the crude hydrocarbon boiling at 80—81°.

This process is applicable to toluene, but the results are less satisfactory. M. O. F.

Tertiary Parabutyltoluene and its Nitro-derivatives. By M. Bialobrzeski (*Ber.*, 1897, **30**, 1773—1776).—The action of aluminium chloride on a mixture of toluene and butylic haloid gives rise to tertiary butyltoluene, alike whether the tertiary or iso-alkylic derivative is employed (Baur, Abstr., 1894, i, 446), and the author finds that ferric chloride effects the same result, involving rearrangement and conversion of the isobutylic into the tertiary butylic radicle. Whilst, however, the hydrocarbon obtained by Baur yields metabutylbenzoic and isophthalic acids on oxidation, and is therefore metabutyltoluene, the product of the action of ferric chloride is converted into parabutylbenzoic and terephthalic acids on oxidation, and must be therefore regarded as the para-derivative.

Tertiary parabutyltoluene, $C_6H_4Me\cdot C_4H_9$, boils at 189—190° under a pressure of 758 mm., and has the sp. gr. = 0·8784 and 0·8611 at 0° and 23° respectively. The *dinitro*-derivative crystallises from dilute alcohol, and melts at 94—95°; it has a feeble odour of musk. M. O. F.

Trihydroxyphenylenic Bisulphide. By P. Genvresse (*Bull. Soc. Chim.*, 1897, [iii], **15**, 1038—1048. Compare this vol., i, 240).—The author is disposed to regard thianthrene (Kraft and Lyons, Abstr., 1896, i, 297) as having the sulphur atoms in the meta-position, Zorn and Brunel (Abstr., 1895, i, 287) having shown that in aromatic sulphones the group SO_2 is in the meta-position; moreover, hexamethyldiphenylene bisulphide may be prepared from mesitylene in presence of excess of the hydrocarbon.

Hexamethyldiphenylene bisulphide, $C_6HMe_3{:}(S)_2{:}C_6HMe_3$, is prepared by heating mesitylene with sulphur and aluminium chloride during 6 hours. It boils, and in part decomposes, at 275° under a pressure of 15 mm.; it is a viscous liquid, and gives a red coloration with concentrated sulphuric acid.

Hexamethyldiphenylene disulphone, $C_6HMe_3{:}(SO_2)_2{:}C_6HMe_3$, is obtained by oxidising the bisulphide with chromic acid in glacial acetic acid, and forms yellowish-white crystals; it decomposes above 300° without undergoing fusion.

The phenolic character of trihydroxyphenylenic bisulphide has been already indicated (this vol., i, 240). The *mono-silver* derivative separates from the aqueous solution in reddish-black crystals. The phthalic anhydride *compound*, $C_{20}H_8S_4O_7$, is obtained by heating trihydroxydiphenylenic bisulphide with phthalic anhydride in sealed tubes at 200° during 10 hours; it is an amorphous substance, dissolves readily in alkalis, and melts at 185°. The alcoholic solution dyes cotton pale red. M. O. F.

Phthalyl and Succinyl Ethers of Eugenol. By M. Rogoff (*Ber.*, 1897, **30**, 1795—1796).—The *succinyl* derivative of eugenol is obtained by heating eugenol with succinic chloride during 4 hours on the water bath, and crystallising the product from glacial acetic acid; it melts at 89·5—90°; aniline forms succinanilide when heated with the substance on the water bath, and phenylhydrazine gives rise to the succinyl derivative. The *phthalyl* derivative of eugenol crystallises in needles, and melts at 98·5—99°; phthalanil is formed under the influence of aniline, but phenylhydrazine has no action on the substance.

M. O. F.

Mixed Amidines. By HANS VON PECHMANN (*Ber.*, 1897, **30**, 1779—1783. Compare Abstr., 1896, i, 31; also the following abstract).—The outcome of previous work on mixed amidines indicates that compounds of the general formulæ, $NX{:}CR{\cdot}NHY$ and $NHX{\cdot}CR{:}NY$, independently of the method of their preparation, occur in one form only, but when X and Y represent chemically similar substituents, this form exhibits tautomerism, inasmuch as methylation gives rise simultaneously to the compounds $NX{:}CR{\cdot}NMeY$ and $NMeX{\cdot}CR{:}NY$; in the case of dissimilar substituents, one alkylic derivative only is produced, the alkylic group becoming attached to the nitrogen atom, with which is combined the substituent of higher molecular weight, and thus establishing the constitution of the original amidine. An exception to the latter generalisation, however, is afforded by phenylbenzylamidine (following abstract), which has the constitution $NHPh{\cdot}CPh{:}N{\cdot}CH_2Ph$.

Phenylbenzenylamidine, $NH{:}CPh{\cdot}NHPh$, was first obtained by Bernthsen, who ascribed to it the foregoing constitution, a conclusion which has been also confirmed by Lottermoser (this vol., i, 38); although treatment of benzanilideimidochloride with ammonia might be expected to yield the isomeric substance $NH_2{\cdot}CPh{:}NPh$, the action in question affords a convenient method of preparing the base. It crystallises from alcohol, and melts at 112°, the hydriodide melting at 169—170°.

Phenylbenzenylmethylamidine, $NH{:}CPh{\cdot}NMePh$, is obtained by the action of methylic iodide at the ordinary temperature; it crystallises from petroleum in colourless, prismatic needles, and melts at 85°. The *hydriodide* and *picrate* melt at 214° and 184° respectively. When heated with methylic iodide, phenylbenzenylamidine yields methylphenylamidobenzenylmethylimidine, which melts at 56° (Abstr., 1896, i, 32).

Hydrolysis with boiling acids or a 20 per cent. solution of caustic soda resolves phenylbenzenylmethylamidimidine into methylaniline, ammonia, and benzoic acid.

The author considers that the recognition of labile modifications of certain mixed diazoamido-compounds, recently described by Hantzsch and F. M. Perkin, has no very secure foundation.

M. O. F.

Mixed Amidines. By HANS VON PECHMANN and BERTHOLD HEINZE (*Ber.*, 1897, **30**, 1783—1789. Compare foregoing abstract). —*β-Naphthylphenylbenzenylamidine*, $NPh{:}CPh{\cdot}NH{\cdot}C_{10}H_7$, or

$$NHPh{\cdot}CPh{:}N{\cdot}C_{10}H_7,$$

produced alike from benzanilide imidochloride and β-naphthylamine, or benzonaphthalide imidochloride, crystallises from dilute alcohol in bright yellow prisms melting at 147°. When heated with methylic iodide for 10 hours at 90—100° in closed vessels, it yields a mixture of *benzenylmethylphenylamido-β-naphthylimidine*, $NMePh\cdot CPh{:}N\cdot C_{10}H_7$, which is obtained from β-benzonaphthalide imidochloride and methylaniline, and melts at 84°, and *benzenylmethyl-β-naphthylamidophenylimidine*, $NPh{:}CPh\cdot NMe\cdot C_{10}H_7$, prepared from benzanilide imidochloride and β-methylnaphthylamine, which melts at 110°; the *hydriodides* of the methyl bases melt at 243° and 230·5° respectively, whilst the mixture of bases obtained on methylating the original amidine melts at 78°, and yields a mixture of hydriodides which melts at 218°. β-Methylnaphthylamine is prepared by heating equal parts of β-naphthylamine and methylic iodide with two parts of wood spirit in sealed tubes for 12 hours at 100°; when regenerated from the nitrosamine, it is a colourless oil which boils at 296° under a pressure of 715 mm. The nitrosamine forms nacreous scales, and melts at 90°.

Metanitrodiphenylbenzenylamidine, $NPh{:}CPh\cdot NH\cdot C_6H_4\cdot NO_2$, or $NHPh\cdot CPh{:}N\cdot C_6H_4\cdot NO_2$, is prepared from benzanilide imidochloride and metanitraniline, as also from benzometanitranilide imidochloride and aniline; it crystallises in lemon-yellow prisms, and melts at 118°. Methylation converts it into a mixture of *benzenylmethylphenylamidometanitrophenylimidine*, $NMePh\cdot CPh{:}N\cdot C_6H_4\cdot NO_2$, obtained from benzonitranilide imidochloride and methylaniline, melting at 107·5°, and *benzenylmethylmetanitrophenylamidophenylimidine*,

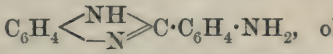
$$NPh{:}CPh\cdot NMe\cdot C_6H_4\cdot NO_2,$$

which is prepared from benzanilide imidochloride and metanitromethylaniline, and melts at 97·5°; the *hydriodides* of these bases melt at 235° and 242° respectively, whilst the mixture of bases obtained on methylating the original amidine melts at 84°, and yields the mixture of hydriodides melting at 224°. *Benzometanitranilide imidochloride*, $CPhCl{:}N\cdot C_6H_4\cdot NO_2$, crystallises from benzene in colourless leaflets or prisms, and melts at 80°.

Phenylbenzylbenzenylamidine, $NHPh\cdot CPh{:}N\cdot CH_2Ph$, which is an exception to the law which states that on alkylating an amidine having chemically dissimilar constituents the alkylic group combines with the substituent of higher molecular weight (foregoing abstract), is obtained from benzanilide imidochloride and benzylamine, and melts at 100°; it was first prepared by Beckmann and Fellrath (Abstr., 1893, i, 203), and the methyl derivative is an individual substance having the constitution $NMePh\cdot CPh{:}N\cdot CH_2Ph$, and melting at 67°. It cannot be prepared from benzoylbenzylamine imidochloride and aniline, however, because the latter converts that substance into benzonitrile and benzylaniline, whilst methylaniline resolves it into benzonitrile and benzylmethylaniline.

Benzoylbenzylamine imidochloride, $CPhCl{:}N\cdot CH_2Ph$, is an oil which boils at 104° and 110° under pressures of 60 mm. and 80 mm. respectively. It fumes in the air, and yields benzoylbenzylamine when treated with water. M. O. F.

Amido-Amidines. By CHARLES LAUTH (*Compt. rend.*, 1897, **124**, 1105—1106).—*Paranitrobenzorthonitranilide*, crystallises from toluene in yellow plates, and is sparingly soluble in alcohol and petroleum ; it melts at 216°.

Paramidobenzenylphenyleneamidine,  $C_6H_4<\substack{NH \\ -N}>C\cdot C_6H_4\cdot NH_2$, obtained on reducing the foregoing compound with hydrochloric acid and tin, forms long, colourless prisms, readily soluble in alcohol, and sparingly soluble in boiling water ; it melts at 240°, and the alcoholic solution exhibits violet dichroism. The *hydrochloride* is sparingly soluble in water, and crystallises in prisms. The base is evidently different from the compound obtained in 1874 by Hubner and Stoever, on nitrating benzenylphenyleneamidine, and reducing the product. Although they describe the substance as melting at 245°, the base obtained by the author on following their instructions melts at 281° ; morever, this compound crystallises in spherical aggregates, and the alcoholic solution exhibits green dichroism, whilst the hydrochloride, which dissolves very readily in water, crystallises in plates.

Both bases when diazotised yield products which combine with amines and phenols, producing similar colouring matters ; these dye cotton direct in shades which vary from yellow to red or black, according to the nature of the amine or phenol. These colours are indifferent towards chemical agents, but fade when exposed to light.

M. O. F.

Compounds of Hydrogen Chloride with Azophenols. By John T. Hewitt and Frank G. Pope (*Ber.*, 1897, **30**, 1624—1630).—The authors describe a number of compounds of hydrogen chloride with different azophenols, most of which have been previously obtained by various chemists, although often not in a state of purity. The compounds were obtained by passing a current of dry hydrogen chloride through a benzene solution of different azophenols.

Benzene azophenol hydrochloride, $NPh\colon N\cdot C_6H_4\cdot OH,HCl$, crystallises in red needles melting and decomposing at 169°. *Orthochlorobenzeneazophenol hydrochloride* crystallises in dark red prisms melting at about 135°. The corresponding *metachloro*-derivative melts and decomposes at 162—164° ; the *para*-compound crystallises in vermilion-red prisms. Orthotolueneazophenol hydrochloride crystallises in minute, dark red needles and prisms softening at 120° and melting at 141°, the para-compound softens at 163°, melts at 169°, and decomposes at 176°. Klein (*Diss. Heidelberg*) gives 172° as the melting point. These hydrochlorides are readily decomposed by water, in most cases yielding the hydrates previously described (Abstr., 1895, i, 353). The hydrochlorides of parachlorobenzeneazophenol and of paratolueneazophenol, however, yield the anhydrous compounds. The authors find that the acetyl, benzoyl, and benzenesulphonyl derivatives of the above azophenols are not capable of combining with hydrogen chloride. The alkylic ethers of the azophenols combine with hydrogen chloride in very much the same way as the azophenols themselves (compare Fischer, *Diss.*). *Benzeneazophenetoil platinochloride*, $(NPh\colon NC_6H_4\cdot OEt)_2,H_2PtCl_6$, melts at 186°.

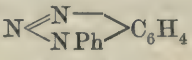
Metachlorobenzeneazophenylic ethylic ether, $C_6H_4Cl\cdot N\colon N\cdot C_6H_4\ OEt$, crystallises in flat, yellow needles melting at 51°, and yields a *platino-*

chloride melting and decomposing at 182°. *Parachlorobenzeneazophenylic methylic ether* crystallises in yellow plates melting at 122°. It is readily soluble in all organic solvents with the exception of light petroleum, and yields a *platinochloride* melting and decomposing at 216°. The corresponding *ethylic ether* crystallises in needles melting at 118°; its *platinochloride* melts and decomposes at 201°. J. J. S.

Azimido-, Aznitroso-, Oxazimido-, Oxaznitroso- and Nitrosazimido-compounds.

By H. CONRAD C. WILLGERODT (*J. pr. Chem.*, 1897, [ii], 55, 375—398).—A satisfactory abstract can hardly be made of this paper; it contains an historical account of the subject, and a list of the compounds prepared by the author and his pupils; a change of view regarding the constitution of these compounds is developed, and proposals are made for a new system of nomenclature to be applied to ring compounds containing nitrogen.

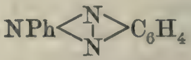
The fact is recalled that the azimides exist in two isomeric forms,



$$\mathrm{N}\lll\begin{smallmatrix}\mathrm{N}-\\ \mathrm{NPh}\end{smallmatrix}>\mathrm{C_6H_4}$$

Azimides.

and

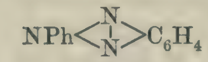


$$\mathrm{NPh}<\begin{smallmatrix}\mathrm{N}\\ |\\ \mathrm{N}\end{smallmatrix}>\mathrm{C_6H_4}$$

Pseudo-azimides.

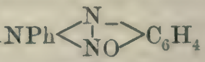
The azimides are obtained by the action of nitrous acid on orthodiamines; they are basic; and, when they have NH in place of NPh, this hydrogen atom can be replaced by metals, acid radicles, or alkyl groups; the compounds formed in the last case can unite with alkylic iodide, forming quaternary ammonium derivatives. The pseudo-azimides are obtained by oxidising orthamido-azo-compounds, or by the decomposition of the diazo-imides obtainable from these; they have no basic properties.

It is next pointed out that what have hitherto been known as di- and mono-nitrosoazo-compounds ought rather to be regarded respectively as nitro-azimido- and azonitroso-compounds, and that the substances obtainable from them by oxidation ought to be regarded as oxazimido- and oxazonitroso-compounds, the trinitrosoazo-compounds being further regarded as nitrosoazimido-compounds. The following may be taken as types of these five classes of compounds, into which the author divides the substances prepared by himself and his pupils:



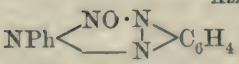
$$\mathrm{NPh}<\begin{smallmatrix}\mathrm{N}\\ |\\ \mathrm{N}\end{smallmatrix}>\mathrm{C_6H_4}$$

Azimido-.



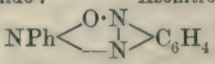
$$\mathrm{NPh}<\begin{smallmatrix}\mathrm{N}-\\ |\\ \mathrm{NO}\end{smallmatrix}>\mathrm{C_6H_4}$$

Azonitroso-.



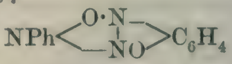
$$\mathrm{NPh}<\begin{smallmatrix}\mathrm{NO\cdot N}\\ |\\ -\!-\!-\mathrm{N}\end{smallmatrix}>\mathrm{C_6H_4}$$

Nitrosoazimido-.



$$\mathrm{NPh}<\begin{smallmatrix}\mathrm{O\cdot N}\\ |\\ -\!-\mathrm{N}\end{smallmatrix}>\mathrm{C_6H_4}$$

Oxazimido-.



$$\mathrm{NPh}<\begin{smallmatrix}\mathrm{O\cdot N}-\\ |\\ -\!-\mathrm{NO}\end{smallmatrix}>\mathrm{C_6H_4}$$

Oxazonitroso-.

These names are read: Phenyleneazimidobenzene, phenyleneazonitrosobenzene, &c. C. F. B.

Combination of Phenylhydrazine with Metallic Chlorides.

By JULES VILLE and JOSEPH MOITESSIER (*Compt. rend.*, 1897, 124, 1242—1244).—When moderately dilute alcoholic solutions of phenylhydrazine are mixed with similar solutions of zinc, nickel, cobalt, cadmium, or magnesium chlorides, compounds are formed of the type

$MCl_2(NHPh{\cdot}NH_2)_2$. The zinc, nickel, and cobalt compounds crystallise in needles, the cadmium and magnesium compounds in prismatic lamellæ. They are only slightly soluble in cold water, but dissolve somewhat easily in boiling water or alcohol; the solutions give the reactions of phenylhydrazine and the particular metallic chloride. When heated, the compounds decompose before they melt. C. H. B.

Symmetrical Carbamides of the Benzene Series. By PAUL CAZENEUVE and MOREAU (*Compt. rend.*, 1897, **124**, 1102—1104. Compare Abstr., 1896, i, 544).—The general method of preparing symmetrical carbamides of the benzene series, recently described by the authors (*loc. cit.*), has been applied in producing the following compounds.

Di-ψ-cumylcarbamide crystallises from a large quantity of boiling alcohol in colourless needles, insoluble in benzene and water, and only sparingly soluble in ether and chloroform; it volatilises at 280° without undergoing fusion.

Dixylylcarbamide [$Me_2 : NH = 1 : 2 : 4$] also crystallises in needles, and is insoluble in water and ether, but dissolves in alcohol, chloroform, benzene, and nitrobenzene; the compound melts at 234—235°. 1 : 2 : 3-Xylidine appears to give rise to two substances, a *dixylylcarbamide* melting at 240—241°, which is insoluble in water and ether, and crystallises in the first fraction from alcohol, and a more readily soluble *dixylylcarbamide*, which melts at 207—209°, and occurs in the alcoholic mother liquor. The *dixylylcarbamide* [$Me_2 : NH = 1 : 4 : 2$] is insoluble in water, cold alcohol, benzene, and ether; it crystallises from a large quantity of boiling alcohol in needles, and volatilises at 285° without melting.

Diparanisylcarbamide crystallises from alcohol in small, white needles and melts at 231—232°. The ortho-compound melts at 182—183°, and not at 174°, as stated by Mulhäuser.

Fatty amines and primary hydrazines also yield carbamides when treated with the carbonic ethers of phenols. M. O. F.

Pentaphenylbiguanide. By J. F. CARL SCHALL (*J. pr. Chem.*, 1897, [ii], **55**, 416).—This substance was described by the author in a communication to the Zurich Chemical Society, before Marckwald described it (Abstr., 1896, i, 30). He will shortly publish a paper on carbodiphenylamide derivatives. C. F. B.

New Synthesis of Aromatic Aldehydes. By LUDWIG GATTERMANN and J. A. KOCH (*Ber.*, 1897, **30**, 1622—1624).—The authors have succeeded in synthesing aromatic aldehydes by passing carbonic oxide and hydrogen chloride into different hydrocarbons in which aluminium chloride and cuprous chloride are suspended. Aldehydes have in this way been obtained from toluene, ortho-, meta-, and para-xylene, ethylbenzene, mesitylene, &c.

A mixture of toluene (30 grams), finely divided, fresh aluminium chloride (45 grams), and cuprous chloride (4 grams) is kept well stirred at a temperature of 20—25°, and through it a mixture of carbonic oxide and hydrogen chloride is kept passing. The carbonic oxide issues from a 10 litre gasholder, and it should take about 3 hours for the whole to pass through the liquid. About 3 litres are absorbed and the unused portion can be collected and again passed through the mixture. The current of hydrogen chloride should be about half as strong as that of the carbonic oxide. The dark product is poured on to ice, and the aldehyde and any unaltered toluene are driven over with steam; they can then be separated by prolonged shaking with sodium hydrogen sulphite solution. After removing the undissolved toluene by means of a separating funnel, the paratolyl aldehyde can be liberated from the solution by treatment with anhydrous sodium carbonate and purified by distillation with steam. The yield is good.

J. J. S.

Reduction of Aromatic Nitro-derivatives. By ALFRED KIRPAL (*Ber.*, 1897, 30, 1597—1600).—Bamberger and Friedmann (Abstr., 1895, i, 217) have shown that when metanitrobenzaldehyde is reduced in aqueous solution with zinc dust, a condensation product of the hydroxylamine derivative, and not this derivative itself, is formed. This condensation product, on oxidation, yields metanitrosobenzaldehyde. The author finds that when paranitrobenzaldehyde is reduced in a similar manner neither the hydroxylamine derivate nor a condensation product of this is formed. The product obtained is an extremely unstable substance which is readily oxidised by the atmospheric oxygen to *parazoxybenzaldehyde.* This crystallises from light petroleum or from benzene in yellow needles melting at 194°. Its *phenylhydrazone* crystallises from hot acetone in reddish-yellow needles melting and decomposing at 230°. When oxidised with potassium dichromate and dilute sulphuric acid, the aldehyde yields *parazoxybenzoic acid.* This acid is practically insoluble in all the usual solvents and decomposes at 240°.

J. J. S.

Organic Syntheses depending on Elimination of Halogen Hydride by means of Ferric Chloride. By MARCELLUS NENCKI (*Ber.*, 1897, 30, 1766—1768).—A description is given of numerous experiments which indicate the value of sublimed ferric chloride as a condensing agent. Its action in general is much milder than that of aluminium chloride, rendering it applicable to syntheses which cannot be effected by this agent.

It is only halogen derivatives which lend themselves to syntheses by means of ferric chloride. Hydroxyketones, for example, are not produced by the action of the substance on acidyl hydrates and phenols, although the use of zinc chloride brings about this result; it is usual to add, in small quantities, one molecular proportion of the condensing agent to the hydrocarbon or phenol, in presence of the acidyl chloride, which will yield the required ketone. In some cases, however, a very small quantity of ferric chloride is sufficient to set up vigorous evolution of hydrogen chloride from a mixture of chloride and hydrocarbon.

When it is required to prepare a hydroxyketone from a polyhydric phenol, it is necessary to employ as many molecular proportions of the acidyl chloride in excess of the theoretical number as will suffice to etherify the hydroxylic groups; for example, in preparing acetophloroglucinol, $COMe\cdot C_6H_2(OH)_3$, four molecular proportions of acetic chloride must be used.

As in the case of aluminium chloride, halogen compounds give better results with hydrocarbons than with phenols or carboxylic acids, whilst nitrophenol is altogether without action; moreover, acidyl chlorides are more active than alkylic chlorides. In the case of certain phenols, the action of ferric chloride in presence of acidyl chlorides gives rise to diketones; thus resacetophenone, $(COMe)_2C_6H_2(OH)_2$, and gallodiacetophenone, $(COMe)_2C_6H(OH)_3$, are formed from acetic chloride and resorcinol and pyrogallol respectively. M. O. F.

Action of Acidyl Chlorides on Benzene and Monhydric Phenols in Presence of Ferric Chloride. By MARCELLUS NENCKI and E. STOEBER (*Ber.*, 1897, 30, 1768—1772. Compare foregoing abstract).—When sublimed ferric chloride (7 parts) is added in small quantities to a mixture of benzene (5 parts) and benzoic chloride (7 parts), hydrogen chloride is liberated in considerable volume, and the liquid finally crystallises; the yield of benzophenone amounts to 70 per cent. of the theoretical amount, and an equally satisfactory return of acetophenone is made on using acetic chloride, carbon bisulphide in this case being employed as diluent, and the operation carried out in a reflux apparatus.

Parahydroxyacetophenone is prepared from phenol and acetic chloride; it melts at 108°, and develops a reddish-violet coloration with ferric chloride (compare Klingel, Abstr., 1886, 60). The phenylhydrazone melts at 136°. 1 : 2 : 5- and 1 : 3 : 6-Methylhydroxyacetophenones are produced from acetic chloride with ortho- and meta-cresol respectively, whilst phenol and benzoic chloride fail to yield hydroxybenzophenone, the product consisting of the benzoyl ether of phenol.

Ortho- and para-chlorhydroxyacetophenones are prepared from acetic chloride and ortho- and para-chlorophenols respectively; orthochlorhydroxybenzophenone results from orthochlorophenol and benzoic chloride.

The red colouring matter, $C_{14}H_{10}O_3$, obtained by Bourquin from salicylaldehyde and zinc chloride (Abstr., 1884, 1164) is also produced by the action of ferric chloride. M. O. F.

Halogen-substituted Ketones. By FRANZ KUNCKELL (*Ber.*, 1897, 30, 1713—1714. Compare this vol., i, 282).—*Orthoxylyl chloromethyl ketone*, $CH_2Cl\cdot CO\cdot C_6H_3Me_2$, crystallises in colourless needles melting at 73—74°, and is readily soluble in alcohol or ether. *Chloromethyl ψ-cumyl ketone* crystallises in colourless plates melting at 76°. By treating toluene with bromacetic bromide according to the method previously given, the author has obtained the same brominated ketone as was previously prepared by the action of bromine on tolyl methyl ketone. *ψ-Cumyl bromomethyl ketone*, $CH_2Br\cdot CO\cdot C_6H_2Me_3$, is obtained when a mixture of ψ-cumene (1·2 part) and bromacetic bromide (3 parts) is added drop by drop to dry carbon bisulphide in which aluminium chloride (3 parts) is suspended. The mixture is kept at the ordinary temperature and then poured into water. The ketone crystallises from its alcoholic solution in colourless prisms melting at 56°.

Pentethylphenyl bromomethyl ketone, $CH_2Br\cdot CO\cdot C_6Et_5$, crystallises in colourless needles and melts at 86°. J. J. S.

Action of Chloracetic Chloride on Phenol and its Ethers. By Franz Kunckell and Friedrich Johannsen (*Ber.*, 1897, **30**, 1714—1716).—Phenylic chloracetate is obtained when aluminium chloride (50 grams) is gradually added to a mixture of phenol (50 grams), and chloracetic chloride (60 grams) diluted with 1½ times its volume of carbon bisulphide. The mixture is allowed to remain for some time and, is then poured into ice cold water. When double the quantities of acetic chloride and of aluminium chloride given above are used, the chief product is a *parachloromethyl ketone* of *phenylic chloracetate*, $CH_2Cl{\cdot}CO{\cdot}C_6H_4{\cdot}O{\cdot}CO{\cdot}CH_2Cl$ $[CO:O = 1:4]$. It crystallises from alcohol in colourless needles, melts at 104°, and is readily soluble in chloroform.

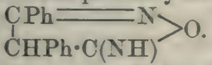
Paranisyl chloromethyl ketone, $OMe{\cdot}C_6H_4{\cdot}CO{\cdot}CH_2Cl$, is obtained in a similar manner by adding aluminium chloride (22·5 grams) to anisoil (15 grams) and chloracetic chloride (22·5 grams) diluted with carbon bisulphide. It crystallises in colourless needles melting at 102°, and when oxidised with potassium permanganate yields anisic acid. When double the above quantities of aluminium chloride and chloracetic chloride are used, *anisyldichlormethyl diketone* (dichloracetylanisoil) $OMe{\cdot}C_6H_3(CO{\cdot}CH_2Cl)_2$, melting at 106° is obtained.

Parabromanisyl chloromethyl ketone, $OMe{\cdot}C_6H_3Br{\cdot}CO{\cdot}CH_2Cl$ $[OMe:Br = 1:4]$, crystallises in needles melting at 94°.

Phenetyldichloromethyl diketone, $OEt{\cdot}C_6H_3(CO{\cdot}CH_2Cl)_2$, crystallises in white plates melting at 108°. Neither of the two diketones are acted on by potassium permanganate. J. J. S.

Action of α-Bromobutyric Chloride on Benzene in the Presence of Aluminium Chloride. By A. Collet (*Bull. Soc. Chim.*, 1896, [iii], **15**, 1100—1103).—A mixture of α-bromobutyric chloride (50 grams) and dry benzene (200 grams) is gradually added to finely powdered aluminium chloride (75—80 grams) and the action is completed by warming on the water bath. The purified product distils at 154—158° under a pressure of 20 mm. It is a slightly yellow, oily liquid with an irritating odour, and has the composition of phenyl bromopropyl ketone, $CH_2Me{\cdot}CHBr{\cdot}CO{\cdot}C_6H_5$. It reacts with aniline to yield an *anilide*, $CH_2Me{\cdot}CH(NHPh){\cdot}COPh$, melting at 85—86°. The *anilide hydrochloride* is precipitated as a white powder when hydrogen chloride is passed into an ethereal solution of the anilide. The *orthotoluidide* melts at 91°, and the *paratoluidide* at 96°.
J. J. S.

Condensation of Ethylic Salts and Cyanides by Means of Sodium Ethoxide. By Reinhold Walther, and P. G. Schickler, (*J. pr. Chem.*, 1897, [ii], **55**, 305—356).—The reaction was carried out by adding dry sodium ethoxide to the ethylic salt (sometimes in ethereal solution) and finally adding the cyanide; sometimes it was found desirable to keep the mixture cool, at others the reaction was promoted by warming. Occasionally, a mixture of the ethylic salt and the cyanide was added to dry sodium ethoxide; and the whole was sometimes heated in a sealed tube. Water was eventually added to the product, unchanged ethylic salt and cyanide removed by extraction with ether, the residue acidified, and the crude product then extracted with ether. The normal reaction is the formation of a cyanoketone; for example, $R\cdot COOEt + CH_2R'\cdot CN = R\cdot CO\cdot CHR'\cdot CN + EtOH$. The cyanoketones are readily hydrolysed by alkalis to the acid R·COOH and the original cyanide $R'\cdot CH_2\cdot CN$; heating with concentrated hydrochloric acid at 150° sometimes converts them into the ketones $R\cdot CO\cdot CH_2R'$.

Ethylic benzoate could not be made to condense with ethylic cyanide, except that perhaps a small amount of condensation occurred when the two substances were heated for 5 hours at 150° with sodium ethoxide. With benzylic cyanide, however, ethylic benzoate condenses with comparative ease, the yield being 10—20 per cent. of the theoretical. The product, phenyl cyanobenzyl ketone (cyanodeoxybenzoin), CPhO·CHPh·CN, which melts at 87—90°, has an atom of hydrogen replaceable by metals; its *phenylhydrazone* melts at 169°, and its *oxime* at 160—162°; as the latter, when heated at 150° with strong hydrochloric acid, yields no product that will reduce silver nitrate, the substance is probably not a true oxime, but rather *diphenylisoxazolonimide*,  $\begin{matrix}\text{CPh}{=\!=\!=}\text{N}\\ \vert\\ \text{CHPh}\cdot\text{C(NH)}\end{matrix}\!\!>\text{O}$. This substance forms, with acetic anhydride, not a mono-, but a *di-acetyl* derivative, melting at 144—145°; in this connection, it may be noticed that phenyl cyanobenzyl ketone itself forms a *monacetyl* derivative melting at 99°. When the cyanoketone is dissolved in alcohol and treated with a drop of ammonia and a little hydrogen peroxide, no amide is obtained, but a substance melting at 95—96°, possibly a physical isomeride of the ketone.

Deoxybenzoincarboxylamide, $CPhO\cdot CHPh\cdot CONH_2$, can, however, be obtained by dissolving the cyanoketone in sulphuric acid diluted with one-tenth of its volume of water and heating to 120°; it melts at 172—173°. Deoxybenzoincarboxylic acid could not be obtained from the amide in a pure state; its *oxime*, melting at 138—139°, and *phenylhydrazone*, melting gradually between 85° and 150°, can, however, be obtained by treating the amide with hydroxylamine and phenylhydrazine; its *ethylic* salt (hitherto obtained in another way as an oil) melts at 90°. When cyanodeoxybenzoin is treated with diazobenzene chloride, the product is *benzeneazodeoxybenzoin*,

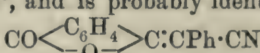
$$CPhO\cdot CHPh\cdot N_2Ph;$$

it is yellow, and melts at 159°. By passing dry gaseous ammonia for 15 minutes over cyanodeoxybenzoin heated to 160—170° in a U-tube, *imidobenzoylbenzylcyanide* (*phenacetobenzodinitrile*),

$$NH{:}CPh\cdot CHPh\cdot CN,$$

is formed; this melts at 146°. It is probably formed in small quantity when a mixture of phenylic and benzylic cyanides is treated with sodium, for when the product is dissolved in alcohol and the solution saturated with gaseous hydrogen chloride, some ethylic deoxybenzoincarboxylate (see above) is formed.

Ethylic orthochlorobenzoate hardly condenses, if at all, with benzylic cyanide. The same is true of the metabromobenzoate. Ethylic orthonitrobenzoate yields a small quantity of a product that melts and decomposes at 225—230°, and forms a yellow substance, melting at 80°, when heated with strong hydrochloric acid at 150°; the reaction is probably not normal. With ethylic metanitrobenzoate, no result was obtained.

With ethylic phthalate, however, benzylic cyanide does yield a product which melts at 164°, and is probably identical with Gabriel's cyanobenzylidenephthalide,  $CO<\begin{smallmatrix}C_6H_4\\ -O-\end{smallmatrix}>C\colon CPh\cdot CN$ (Abstr., 1885, 902). With ethylic formate, it also reacts, but the product in this case, *hydroxymethylenebenzylic cyanide* (*phenylcyanohydroxyethylene*),

$$OH\cdot CH\colon CPh\cdot CN,$$

melting at 157—158°, is probably not a ketone, for it has the reactions of an hydroxy-compound. Strong hydrochloric acid at 150° converts it into phenylacetic acid, ammonia, carbonic oxide, and carbonic anhydride; when oxidised with permanganate in the cold, it yields carbonic anhydride, benzoic acid, and ammonia; with ammonia gas at 160°, it yields yellow *diphenylcyanovinylamine*,

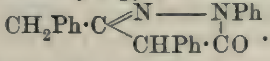
$$NH(CH\colon CPh\cdot CN)_2,$$

which melts at 175°, and regenerates the original substance when boiled with dilute hydrochloric acid. When treated with methylamine in the same way, it apparently forms some of the analogous *methyl* compound, $NMe(CH\colon CPh\cdot CN)_2$, melting at 88—89°; but if mixed in alcoholic solution with methylamine hydrochloride, it forms a compound, $NHMe\cdot CH\colon CPh\cdot CN$, melting at 73—75°, and with aniline in alcoholic solution it forms a yellowish compound, $NHPh\cdot CH\colon CPh\cdot CN$, melting at 155—156°; the last compound, when treated with nitrous acid, forms a yellow and a red substance,, melting and decomposing at 51° and about 107—110° respectively, but neither of these is the normal nitroso-derivative. Hydroxymethylenebenzylic cyanide further forms a *benzoyl* derivative, melting at 116—117°; with phosphoric chloride, it yields a product which melts at 186—187°, and has possibly the constitution $C_2(CPh\cdot CN)_2$, since it contains no chlorine. With hydroxylamine, it forms a product which melts at 98°, and is apparently an *hydroxyamido*-compound, $OH\cdot NH\cdot CH\colon CPh\cdot CN$. Its *methylic* salt melts at 90°; its *ethylic* salt was not obtained pure. When heated with diazobenzene chloride, it yields yellow crystals melting at 147—148°.

With ethylic acetate, benzylic cyanide forms *cyanobenzyl methyl ketone* (*acetobenzylic cyanide*), $CMeO\cdot CHPh\cdot CN$; this melts at 89—90°, and with hydroxylamine yields *phenylmethylisoxazolonimide*, melting at 112—113°. With ethylic propionate, *cyanobenzyl ethyl ketone*, $CEtO\cdot CHPh\cdot CN$, melting at 58°, is formed; *phenylethylisoxazolonimide* melts at 70—71°. *Cyanobenzyl propyl ketone*, $CPr^aO\cdot CHPh\cdot CN$, was obtained as an oil; *phenylpropylisoxazolonimide* melts at 107—108°.

Cinnamoylbenzylic cyanide, $CHPh\colon CH\cdot CO\cdot CHPh\cdot CN + H_2O$, from ethylic cinnamate, benzylic cyanide and sodium ethoxide, is yellow, and melts at 162—163°; by passing hydrogen chloride into its methyl alcoholic solution, *methylic cinnamoylphenylacetate* is obtained.

Methylic cyanide will not condense with ethylic phenylacetate, benzylic cyanide, however, does, forming *phenacetobenzylic cyanide* (*cyanodibenzyl ketone*), $CH_2Ph\cdot CO\cdot CHPh\cdot CN$; this melts at 85—86°. It is reduced by sodium to phenylacetic acid; and with ammonia gas at 170°, it appears to yield dibenzylic cyanide, for the product forms with hydroxylamine hydrochloride a compound melting at 104—107°. With hydroxylamine hydrochloride in alcoholic solution, it yields *phenylbenzylisoxazolonimide,* which melts at 107—108°, and forms a *hydrochloride* when treated with gaseous hydrogen chloride in ethereal solution. With phenylhydrazine, it yields a compound melting at 119—120°. When dissolved in methylic or ethylic alcohol and treated with gaseous hydrogen chloride, it forms *methylic,* or *ethylic, phenacetophenylacetate,* melting at 66—67° and 77—78° respectively. The *amide* of this acid is obtained by dissolving the cyanide in glacial acetic acid and passing in gaseous hydrogen chloride; it melts at 162—164°, and, when treated with phenylhydrazine acetate in alcoholic or acetic acid solution, forms a compound which melts at about 227°, and is presumably a pyrazolone derivative,



$$CH_2Ph\cdot C{<}\begin{array}{l}N\text{——}NPh\\ \qquad\quad\ |\\ CHPh\cdot CO\end{array}.$$

C. F. B.

Quinone-orthamidobenzoic Acid. By Charles Astre (*Bull. Soc. Chim.*, 1897, [iii], **15**, 1025—1027. Compare Abstr., 1895, i, 533).—From the purple liquid which deposits quinone-bis-amidobenzoic acid (*loc. cit.*), a more readily soluble product has been separated.

Quinone-orthamidobenzoic acid, $C_6H_3O_2\cdot NH\cdot C_6H_4\cdot COOH$, is obtained by evaporating the alcoholic filtrate from quinone-bis-amidobenzoic acid, and treating the residue with ethylic acetate, which dissolves the substance readily; the compound is black. M. O. F.

Action of Orthamidobenzoic Acid on Trichloroquinone. By Charles Astre (*Bull. Soc. Chim.*, 1897, [iii], **15**, 1027—1029. Compare Abstr., 1895, i, 533).—*Dichloroquinone-bis-orthamidobenzoic acid,* $C_6Cl_2O_2(NH\cdot C_6H_4\cdot COOH)_2$, is prepared by heating a solution of trichloroquinone in equal parts of alcohol and ethylic acetate with orthamidobenzoic acid dissolved in the same medium for 6 hours at 70—80°; it forms slender needles, and softens at about 300°. The solution in alcohol and ethylic acetate is greenish-yellow. M. O. F.

Action of Orthamidocinnamic Acid on Trichloroquinone. By Charles Astre and H. Stévignon (*Bull. Soc. Chim.*, 1897, [iii], **15**, 1029—1034. Compare Abstr., 1895, i, 533).—*Dichloroquinone-bis-orthamidocinnamic acid,* $C_6Cl_2O_2(NH\cdot C_6H_4\cdot CH{:}CH\cdot COOH)_2$, is obtained by heating trichloroquinone dissolved in equal parts of alcohol and ethylic acetate with orthamidocinnamic acid dissolved in the same medium; the liquid becomes violet, and soon deposits the substance as an amorphous powder, which decomposes before melting. It is insoluble in neutral solvents, and the solution in concentrated sulphuric acid is violet.

Trichloroquinone-orthamidocinnamic acid,

$$C_6Cl_3O_2\cdot NH\cdot C_6H_4\cdot CH{:}CH\cdot COOH,$$

is produced along with the foregoing substance, and is obtained by evaporating the filtrate. It is a black powder, and softens at about 55°.

Dichloroquinone-orthimidocinnamic-bis-orthamidocinnamic acid,

$$COOH\cdot CH{:}CH\cdot C_6H_4\cdot N{:}C_6Cl_2O(NH\cdot C_6H_4\cdot CH{:}CH\cdot COOH)_2,$$

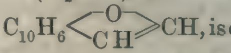
is prepared by heating trichloroquinone with orthamidocinnamic acid in glacial acetic acid; the purple liquid is filtered from dichloro quinone-bis-orthamidocinnamic acid, and evaporated, the residue being washed with boiling water. It is a reddish-brown, amorphous powder.

M. O. F.

Syntheses of Coumarone and of Coumarone Derivatives from Phenoxyacetals. By RICHARD STOERMER (*Ber.*, 1897, 30, 1700—1711.)—In consequence of Hesse's work (this vol., i, 457), the author publishes the following preliminary account of his own researches.

[WITH GIESEKE.] — *β-Naphthoxyacetal*, $C_{10}H_7·O·CH_2·CH(OEt)_2$, obtained by heating β-naphthol (9·4 grams), chloracetal (10 grams), and the requisite quantity of sodium ethoxide for 6 hours at 160—170°, is a heavy, colourless oil, boiling at 206—207° (17 mm. pressure), and of sp. gr. = 1·0654 at 14°.

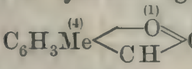
β-Naphthoxyacetaldehyde hydrate, $C_{10}H_7·O·CH_2·CH(OH)_2$, obtained by Pomeranz's method, crystallises from its aqueous solution in colourless needles, melts at 87°, and is readily soluble in ether, alcohol, and benzene. It readily reduces both Fehling's solution and also ammoniacal silver nitrate, but is not volatile with steam. Its *semicarbazone* melts at 182°, its *phenylhydrazone* at 145°, and its *oxime* at 123·5°.

β-Naphthoxyacetonitrile, $C_{10}H_7·O·CH_2·CN$, was prepared by the action of acetic anhydride on the above oxime according to Lach's method (Abstr., 1884, 1154). When the aldehyde (1 part) is heated to boiling with a solution of zinc chloride (3 parts) in acetic acid (10 parts) for 10 minutes, *β-naphtho-α-furan*,  $C_{10}H_6{<}\begin{smallmatrix}O\\CH\end{smallmatrix}{>}CH$, is obtained. It may be readily purified by distillation in steam, and then forms colourless, glistening needles melting at 60—61°. Hesse (*loc. cit.*) gives the melting point as 65°. It yields a *picrate* crystallising in reddish-yellow needles and melting at 141°. *β-Naphthofurancarboxylic acid*, $C_{10}H_6{<}\begin{smallmatrix}O\\CH\end{smallmatrix}{>}C·COOH$, forms colourless crystals melting at 191—192°, and is readily soluble in ether, alcohol, and benzene.

α-Naphthoxyacetal is also an oil, boiling at 207—208° (18 mm. pressure), of sp. gr. = 1·0698 at 14° and $n_D = 1·561$ at 16°. The corresponding *aldehyde* melts at 86° and yields a *semicarbazone* (m. p. 149—150°), a *phenylhydrazone*, and an *oxime* (m. p. 108°). α-Naphthofuran, contrary to Hesse's statement, could only be obtained as an oil of sp. gr. = 1·1504 at 14°; it yields a *picrate* melting at 113°.

Coumarone itself has been synthesised by heating phenoxyacetaldehyde with a solution of zinc chloride in glacial acetic acid.

[WITH H. SCHMIDT.]—The following compounds, which have also been obtained by Hesse, have been prepared, but in most cases the melting and boiling points do not agree with those given by Hesse. Paratolyloxyacetal boils at 270° at the ordinary pressure, but at the same time undergoes slight decomposition; at 20° mm. pressure, its boiling point is 157—158° and its sp. gr. = 0·9959 at 22°. Hesse gives the boiling point at 262—263°. Paratolyloxyacetaldehyde hydrate melts at 58° (Hesse 65°), and the *aldehyde* itself, $C_6H_4Me·O·CH_2·COH$, obtained by heating the hydrate under reduced pressure, distils at 126° under 27 mm. pressure. The semicarbazone melts at 177°, the phenylhydrazone at 111° (Hesse 106°), and the oxime at 99° (Hesse 68°). The oxime, when boiled with acetic anhydride, yields *paratolyloxyacetonitrile*, $C_6H_4Me\cdot O\cdot CH_2\cdot CN$, which crystallises in large, broad needles melting at 40°. Metatolyloxyacetal is an oil boiling at 267—268° (Hesse 262—263°), and its sp. gr. = 0·9728 at 14°. Metatolyloxyacetaldehyde hydrate melts at 57° (Hesse 56°), and its oxime at 87° (Hesse 82°). *Metatolyloxyacetonitrile* is a yellow liquid boiling at 254°. *Orthotolyloxyacetal* boils at 262°, and its sp. gr. = 0·9928 at 22°; the *aldehyde hydrate* forms colourless needles melting at 74°, and has the same objectionable odour as its isomerides; the *semicarbazone* melts at 151°, and the *oxime* at 117°.

By heating each of the three tolyloxyacetals (1 part) separately with a solution of zinc chloride (3 parts) in glacial acetic acid (10 parts), the authors have succeeded in synthesising the three methylcoumarones. *Paramethylcoumarone*,  $C_6H_3\overset{(4)}{Me}\Big\langle\begin{matrix}\overset{(1)}{O}\\ CH\end{matrix}\Big\rangle CH$, is a colourless oil, boiling at 197—199°, of sp. gr. = 1·0467 at 15°, and refractive index = 1·547 at 16°. With sulphuric acid, it yields a dark, brown-red coloration, and its *picrate* crystallises in yellow needles melting at 73°. *Metamethylcoumarone* is also an oil boiling at 195—196°; its sp. gr. = 1·056 at 16°, and its refractive index = 1·554 at 16°. With sulphuric acid, it yields a brilliant, dark purple coloration, and its *picrate* melts at 72°. *Orthomethylcoumarone* boils at 190—191°, and yields a *picrate* melting at 109°.

[With SCHROEDER.]—*Unsymmetrical ortho-xylenoxyacetal*,

$$C_6H_3Me_2\cdot O\cdot CH_2\cdot CH(OEt)_2\ [Me_2 : O = 1 : 2 : 4],$$

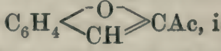
boils under 20 mm. pressure at 168°, and its sp. gr. = 0·992 at 16°. The corresponding *aldehyde hydrate*, $C_6H_3Me_2\cdot O\cdot CH_2\cdot CH(OH)_2$, has an extremely strong odour, melts at 38°, and is readily soluble in water, alcohol, or ether. The *oxime* melts at 99°, the *phenylhydrazone* at 68°, and the *semicarbazone* at 187°. *Unsymmetrical metaxylenoxyacetal* $[Me_2 : O = 1 : 3 : 4]$ boils at 273°, and its sp. gr. = 0·995 at 16°. The *aldehyde hydrate* has a strong odour of lemons, and melts at 62°. The *oxime* melts at 98°, the *phenylhydrazone* at 91—92°, and the *semicarbazone* at 116—117°. *Paraxylenoxyacetal* $[Me_2 : O = 1 : 4 : 2]$ boils at 278—279°, and its sp. gr. = 0·972 at 16°; the *aldehyde hydrate* melts at 63—64°, the *oxime* at 114°, and the *semicarbazone* at 104°.

Parethylphenoxyacetal, $C_6H_4Et\cdot O\cdot CH_2\cdot CH(OEt)_2$ $[Et : O = 1 : 4]$, distils at 288—289°, and when boiled with very dilute sulphuric acid yields *parethylphenoxyacetaldehyde hydrate* melting at 49°, the *oxime* of which melts at 104°.

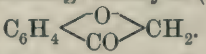
Metaparadimethylcoumarone, obtained from the unsymmetrical ortho-xylenoxyacetal, boils at 221°, its sp. gr. = 1·06 at 15°, and with concentrated sulphuric acid it gives a claret coloration. Its *picrate* melts at 65—66°. *Orthoparadimethylcoumarone* is an oil with a penetrating odour, and boils at 221—222°. At 16°, its sp. gr. = 1·036, and its refractive index 1·5412; with concentrated sulphuric acid, it gives a methyl-violet coloration. Its *picrate* melts at 78—79°. *Orthometadimethylcoumarone* boils at 216°, its sp. gr. = 1·041 at 16°, and its refractive index = 1·549 at the same temperature. Its *picrate* melts at 101°. *Parethylcoumarone* boils at 217—218°, and with sulphuric acid gives a bluish-pink coloration.

ψ-Cumenoxyacetal, $C_6H_2Me_3 \cdot O \cdot CH_2 \cdot CH(OEt)_2$, boils at 290°, and its sp. gr. = 0·9886. The corresponding *aldehyde hydrate* melts at 81°, and yields an *oxime* melting at 110°.

1′: 3 : 4-*Trimethylcoumarone* is a colourless oil boiling at 236°; it solidifies when cooled, but melts again below 18°. Its sp. gr. = 1·0205 at 21°, and its refractive index at the same temperature = 1·547. It yields a *picrate* melting at 105°. J. J. S.



Further Syntheses of Coumarone Derivatives. By Richard Stoermer (*Ber.*, 1897, **30**, 1711—1712. Compare previous abstract.) —*a-Acetylcoumarone*, $C_6H_4{<}\overset{O}{\underset{CH}{}}{>}CAc$, is obtained by the action of chloracetone on the dry sodium salt of acetaldehyde suspended in benzene. The benzene is distilled off, and then the acetylcoumarone can be purified by steam distillation. It crystallises from its benzene solution in thick plates melting at 74—75°, is readily soluble in most organic solvents, and moderately in water. When fused with potash, it yields coumarone, and when oxidised with potassium permanganate, it yields coumarilic acid; it also reacts with hydroxylamine and phenylhydrazine. Ethylic γ-bromacetate and chloracetaldehyde also appear to react with the sodium derivative of salicylaldehyde. Phenoxyacetic acid, $C_6H_5 \cdot O \cdot CH_2 \cdot COOH$, when treated with a solution of zinc chloride in acetic acid, reacts in very much the same way as the corresponding aldehyde (see previous abstract), and yields ketocoumaran, $C_6H_4{<}\overset{O}{\underset{CO}{}}{>}CH_2$. J. J. S.



Phenylglyceric Acids. By Josef Plöchl and Bertram Mayer (*Ber.*, 1897, **30**, 1600—1614).—Anschütz and Kinicutt (Abstr., 1878, 981; 1879, 644), by treating ethylic dibromohydrocinnamate with silver benzoate and then hydrolysing with alcoholic potash, obtained a phenylglyceric acid melting at 117°. Lipp (Abstr., 1883, 994) obtained a phenylglyceric acid melting at 143—144°, but regarded his acid as identical with Anschütz's since it gave the same dibenzoate when heated with benzoic chloride. Fittig and Ruer obtained the same acid melting at 141—142° by oxidising cinnamic acid in the cold with potassium permanganate (Abstr., 1892, 986). The authors have repeated Anschütz and Kinnicutt's experiments, and find that the acid previously described as melting at 117° really melts at 120—121°. It yields a *phenylhydrazide* melting at 177°, and when treated with fuming hydrobromic acid yields *phenyl-β-bromolactic acid*, $CHPhBr \cdot CH(OH) \cdot COOH$, melting and decomposing at 156—157°. The latter acid is readily soluble in alcohol, ether, or warm chloroform, and only sparingly in benzene or warm water; in the latter case, decomposition readily ensues with the formation of phenylacetaldehyde. When heated at about 40° with acetic anhydride, phenylglyceric acid (m. p. 120—121°) yields a *monacetyl* derivative melting at 158°. The following salts have been prepared in a crystalline form: *Calcium* salt, $(C_9H_9O_4)_2Ca + 3H_2O$; *zinc* salt, with $4H_2O$; *copper* salt, with $2H_2O$, and the *lead* salt. The authors also confirm Fittig and Ruer's work on the phenylglyceric acid melting at 141—142° and find that this acid is quite distinct from the one melting at 120—121°. It yields a *phenylhydrazide* which crystallises from dilute alcohol in yellow prisms melting at 215°. With fuming hydrobromic acid, it yields a phenylbromolactic acid melting at 164—165°, and agreeing with the lactic acid obtained from the isomeric phenylglyceric acid in all its properties with the exception of melting point. The *monacetate* of the acid melting at 141—142° crystallises in glistening scales and melts at 93·5°. *Ethylic phenylglycerate dibenzoate*, obtained from the ethylic salt of the acid melting at 141—142° by the Schotten-Baumann method, crystallises in silky needles melting at 85°. The corresponding derivative of the acid melting at 120—121° melts at 109° (Anschütz and Kinnicutt). The *zinc* salt of the acid melting at 141—142° crystallises with $4H_2O$, the *cadmium* salt also with $4H_2O$ and the *copper* salt with H_2O. The authors find that Lipp's method (*loc. cit.*) gives a good yield of the acid melting at 120—121° and but a small amount of the isomeric acid melting at 141—142°. The fact that Lipp does not mention the acid melting at 120—121° is explained by the fact that it is readily soluble in ether, whereas the isomeric acid is not.

The acid of lower melting point can readily be decomposed into its optically active constituents, either by means of its *strychnine* salt (m. p. 144°), or by the action of *Penicillium glaucum* which destroys the dextro- acid more readily than the lævo-. The two *optically active phenylglyceric* acids crystallise in plates melting at 166—167°. They are much less soluble in water than the racemic acid, and their rotatory powers are respectively $[\alpha]_D = +31·08°$ and $[\alpha]_D = -30·23°$. The *zinc*, *calcium*, and *copper* salts of the two active acids are described; they crystallise much more readily than the salts of the racemic acid. All attempts to decompose the acid melting at 141—142° into optically active constituents have so far failed.

When the ethylic salt of the acid of higher melting point is benzoylated at 150° and the resulting dibenzoate hydrolysed with alcoholic potash, the acid melting at 120—121° is formed. If, on the other hand, the dibenzoate of the ethylic salt obtained from the acid melting at 120—121° is hydrolysed with strong aqueous sodium hydroxide, the acid melting at 141—142° is formed together with a small quantity of the isomeric acid. The authors conclude with a comparison of these acids with the tartaric acids and hydrobenzoins. J. J. S.

Caffetannic Acid. By PAUL CAZENEUVE and E. HADDON (*Compt. rend.*, 1897, **124**, 1458—1460).—Since the investigations of Hlasiwetz, caffetannic acid has been usually regarded as having the formula $C_{15}H_{18}O_8$, but the authors, from a study of the behaviour of the substance towards phenylhydrazine, conclude that it has the composition $C_{21}H_{28}O_{14}$, and ascribe to it the constitutional formula $COOH·CH:CH·C_6H_3(O·C_6H_{11}O_5)_2$.

The *osazone* of caffetannic acid, $C_{45}H_{48}N_8O_{10}$, crystallises in yellow needles very sparingly soluble in alcohol, and melts at 180°; it is insoluble in most media, and is so sparingly soluble in phenol and naphthalene that no determinations of molecular weight have been possible.

The sugar, $C_6H_{12}O_6$, obtained on hydrolysing caffetannic acid, will be described in a subsequent paper. M. O. F.

Caffetannic Acid (Glucosylcaffeic Acid) and its Decomposition into Caffeic Acid, Vinylcatechol, and Catechol. By HERMANN KUNZ-KRAUSE (*Ber.*, 1897, **30**, 1617—1622).—Both caffetannic acid and matétannic acid, when hydrolysed, yield a syrupy sugar and caffeic acid (dihydroxycinnamic acid). This acid, when heated at 200°, readily loses carbonic anhydride, yielding vinylcatechol (3:4-dihydroxycinnamene), the decomposition at this temperature being quantitative. A characteristic reaction for vinylcatechol is the one previously mentioned (*Arch. Pharm.*, 1893, **231**, 635). This reaction is also given by Tiemann and Will's hesperetol or vinylcatechol paramonomethyl ether (Abstr., 1881, 739). The carmine-red coloration with sulphuric acid therefore appears to be characteristic of 3 : 4-dihydroxycinnamene and its ethers. The author has only succeeded in obtaining the vinylcatechol as an amorphous powder; it is a somewhat unstable substance, for when distilled under a pressure of 12 mm. it is decomposed, the chief product being catechol. The author thinks it probable that caffetannic acid is distributed throughout the vegetable kingdom in very much the same manner as choline. J. J. S.

Synthesis of Aromatic Acids and Aldehydes by means of Aluminium Chloride. By LOUIS BOUVEAULT (*Bull. Soc. Chim.*, 1897, [iii], **15**, 1014—1021).—The following method of preparing phenylglyoxylic acid is one of general application in the aromatic series. Crystallised benzene (90 grams) is heated with dry carbon bisulphide (200 grams) and aluminium chloride (140 grams) in a reflux apparatus at 40—50°, and treated with the chloride of monethylic oxalate (136 grams), which is added drop by drop; a crystalline double compound is formed, and on treating this substance with water, ethylic phenylglyoxylate (120—130 grams) is set free. Hydrocarbons, and the alkyl ethers of monhydric and polyhydric phenols may be employed in this method of synthesis, which is not applicable, however, to free phenols or their acidyl derivatives. When phenol ethers are used, it is advantageous to add the aluminium chloride in small quantities at a time to the carbon bisulphide solution containing the chloride of monethylic oxalate. The ethylic phenylglyoxylate (or its homologue) obtained by this process is hydrolysed with a hot 10 per cent. aqueous solution of caustic soda, as the alcoholic agent induces secondary changes.

There is no difficulty in converting phenylglyoxylic and its homologues, $R \cdot CO \cdot COOH$, into the respective acids, $R \cdot COOH$, although transformation into the aldehydes, $R \cdot COH$, is less easy to accomplish. When these compounds are heated alone, carbonic anhydride and oxide are generated, along with a mixture of the acid and aldehyde corresponding to the substance employed; but owing to the almost exclusive production of the acid in most cases, this is not the most satisfactory method of procedure. If the acid is required, it is better to treat the compound with aqueous hydroxylamine hydrochloride, which gives rise to the oxime $R \cdot C(NOH) \cdot COOH$; elimination of carbonic anhydride and water from this compound under the influence of heat converts it into the nitrile $R \cdot CN$, which can be hydrolysed to the acid.

In order to prepare the aldehyde, phenylglyoxylic acid or the homologue is heated with aniline, which forms the compound

$R\cdot C(NPh)\cdot COOH$, and this, at the temperature of the boiling base, passes into the phenylimide $R\cdot CH\vdots NPh$; dissolution of this compound in hot 25 per cent. sulphuric acid eliminates aniline, and sets free the aldehyde.

Attempts have been made to substitute hydrazine and paramidophenol for aniline in the foregoing process. Although these compounds undergo condensation with phenylglyoxylic acid and its derivatives, yielding substances from which carbonic anhydride is eliminated by heat, the yield of aldehyde obtained from the product is very poor.

M. O. F.

Acetylsalicylic Acid. By M. BIALOBRZESKI and MARCELLUS NENCKI (*Ber.*, 1897, 30, 1776—1779).—*Acetylsalicylic acid*,

$$COMe\cdot C_6H_3(OH)\cdot COOH,$$

is obtained by adding small quantities of ferric chloride (100 grams) to a mixture of salicylic acid (80 grams) and acetic chloride (100 grams). It is sparingly soluble in water, and dissolves readily in alcohol, ether, benzene, and chloroform; it melts at 210°, and develops a red coloration with ferric chloride. The *oxime* crystallises in needles, and melts at 175°; ferric chloride develops a violet coloration. The *phenylhydrazone* forms yellow needles, and melts and decomposes at 212°; a violet coloration is produced by ferric chloride with this derivative also. The *sodium* salt crystallises in white plates containing $3H_2O$, and the *potassium* salt forms yellowish, microscopic needles containing $\frac{1}{2}H_2O$; the *ammonium* and *barium* salts contain $1H_2O$ and $2H_2O$ respectively.

The antiseptic action of salicylic acid is considerably impaired by the introduction of the acetyl group into the benzene ring. The growth of yeast cells, typhus bacilli, and erysipelas cocci is unchecked by the substance, and the animal organism suffers no inconvenience from its assimilation.

M. O. F.

Diphenacylcyanacetic Acid. By C. TIMOTHÉE KLOBB (*Bull. Soc. Chim.*, 1897, [iii], 15, 1008—1014. Compare Abstr., 1896, i, 126).—Whilst cold aqueous potash is without action on ethylic diphenacylcyanacetate, the boiling solution gives rise to a secondary action, producing ammonia and diphenacylacetic acid; alcoholic potash, on the other hand, yields a very different product (see below), and the method of hydrolysing ethereal salts of other cyano-acids (*loc. cit.*) must be adopted in the present case.

Diphenacylcyanacetic acid, $(COPh\cdot CH_2)_2C(CN)\cdot COOH$, is obtained by treating an acetone solution of the ethylic salt with the calculated amount of caustic potash dissolved in alcohol; hydrolysis takes place immediately at the ordinary temperature, and the liquid, without delay, is largely diluted, and acidified with sulphuric acid. The acid has a bitter taste, and crystallises in small, colourless prisms melting at 172—174°. Alcoholic potash forms a deep blue solution, aqueous alkalis yielding a pale red solution, which rapidly becomes turbid and deposits a red, flocculent precipitate; cold concentrated sulphuric acid dissolves it without developing colour, but on carefully heating the solution it becomes red, and finally emerald green, whilst a cinnabar-red compound, insoluble in water, but forming a blue solution in alcoholic potash, is precipitated on pouring it into water. The alkali salts slowly become pale red on exposure to light. The *sodium* salt contains $2H_2O$, and forms white, nacreous leaflets; it is difficult to obtain the substance colourless, and its solutions become red when heated. The *ammonium* salt contains $2\frac{1}{2}H_2O$, and the *barium* salt, which is insoluble in water and alcohol, contains $1H_2O$ after being dried in a vacuum.

The *compound*, $C_{18}H_{15}NO_3$, is obtained by adding caustic soda to a boiling solution of ethylic diphenacylcyanacetate, and cooling the liquid by repeated decantation, continuing this process until the blue coloration no longer deepens; the solution is then largely diluted, and acidified with sulphuric acid. The bright red precipitate acquires a darker shade when dried in the desiccator. It is insoluble in water, but dissolves freely in alcohol, ether, chloroform, and benzene, forming solutions which redden blue litmus; bright sunlight decolorises it completely. It becomes brown at 140°, and melts and blackens at about 170°. The solution in concentrated sulphuric acid is emerald green, alcoholic potash developing a blue coloration. The production of this substance from ethylic diphenacylcyanacetate seems to depend on the influence of atmospheric oxygen. M. O. F.

An Additive Compound of Aniline with Ethylic Dicarboxyglutaconate. By MAX GUTHZEIT (*Ber.*, 1897, **30**, 1757—1759).—Ruhemann and Morrell (Abstr., 1895, i, 20), and simultaneously Band (Abstr., 1895, i, 561), have shown that aniline resolves ethylic dicarboxyglutaconate into ethylic malonate and ethylic anilidoethylenedicarboxylate; by suitably modifying the conditions of the experiment, the author has isolated the intermediate product of the action.

Ethylic β-anilidodicarboxyglutarate,

$$(COOEt)_2CH\cdot CH(NHPh)\cdot CH(COOEt)_2,$$

is obtained by gradually adding ice-cold aniline (3—5 mols.) to a well cooled 14 per cent. solution of the ethereal salt in ether, and agitating the liquid during the operation; after 24 hours, the solution is extracted with dilute hydrochloric acid, and the ethereal liquid, on evaporation, deposits an oil which rapidly solidifies. It crystallises from light petroleum in clusters of small prisms, and melts at 46—47°; it is feebly basic, and forms a brownish-red, semi-solid *hydrochloride*, which evolves hydrogen chloride in the desiccator. Although ethylic anilidoethylenedicarboxylate melts at 48°, it differs from the additive compound in crystalline form and in its colour reactions; whilst the former substance dissolved in concentrated sulphuric acid develops a blue coloration with ferric chloride and potassium dichromate, changing to deep red in the latter case, a solution of the additive compound becomes yellow with ferric chloride, and dirty brown with potassium dichromate.

The substance dissolves in cold aniline, and after 14 days the solution contains ethylic malonate and ethylic anilidoethylenedicarboxylate; the same result is in part effected when the ethereal salt is distilled in a current of steam (compare Goldstein, Abstr., 1895, i, 470).

M. O. F.

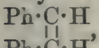
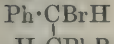
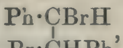
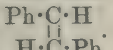
Benzenesulphonamides. By CH. RABAUT (*Bull. Soc. Chim.*, 1897, [iii], **15**, 1035—1037. Compare Abstr., 1895, i, 595).—*Benzene-*

sulphoparatoluidide, $C_6H_5\cdot SO_2\cdot NH\cdot C_6H_4Me$, obtained by the action of benzenesulphonic chloride on paratoluidine, forms white crystals melting at 122° (compare *Ber.*, 1876, **9**, 427). The dinitro-derivative is produced by the action of boiling nitric acid of sp. gr. 1·10, and melts at 178—179°; when heated with concentrated hydrochloric acid in sealed tubes, it yields dinitroparatoluidine (m. p. 166°), so that it is identical with the compound described by Lellman (Abstr., 1883, 800).

Benzenesulphometaxylidine, $C_6H_5\cdot SO_2\cdot NH\cdot C_6H_3Me_2$, dissolves very readily in alcohol, and forms white crystals melting at 128—129°. The *nitro*-derivative [$Me_2 : NH : NO_2 = 1 : 3 : 4 : 5$] is a yellow compound which crystallises from alcohol and melts at 152—153°; concentrated hydrochloric acid converts it into nitrometaxylidine (m. p. 68—69°). The *amido*-derivative forms white needles, and melts at 140—141°.

Benzenesulphoparaxylidine forms white crystals melting at 138—139°. The *dinitro*-derivative is obtained by the prolonged action of boiling nitric acid of sp. gr. 1·10, and melts at 174—175°. The *diamido*-derivative separates in white crystals which become brown in air; it melts at 180—181°.

These sulphonamides are readily oxidised by potassium permanganate. M. O. F.

The Second Stilbene. By ROBERT OTTO and FRITZ STOFFEL (*Ber.*, 1897, **30**, 1799—1800. Compare Abstr., 1896, i, 242).—It has been shown (*loc. cit.*) that α-stilbene dibromide (m. p. 237°) yields stilbene when treated with sodium phenylmercaptide. Wislicenus and Seeler (Abstr., 1896, i, 98) have pointed out that whilst α-stilbene dibromide may be considered to be derived from plane-symmetrical stilbene  $\begin{array}{c}Ph\cdot C\cdot H\\ \| \\ Ph\cdot C\cdot H\end{array}$, and therefore expressed by the meso-tartaric formula  $\begin{array}{c}Ph\cdot CBrH\\ | \\ H\cdot CPhBr\end{array}$, the β- (*iso*) compound (m. p. 110°) probably has the racemic configuration  $\begin{array}{c}Ph\cdot CBrH\\ | \\ Br\cdot CHPh\end{array}$, being derived from the central symmetrical hydrocarbon  $\begin{array}{c}Ph\cdot C\cdot H\\ \| \\ H\cdot C\cdot Ph\end{array}$. Studying the behaviour of the *iso*-dibromide (m. p. 110°) towards sodium phenylmercaptide, the authors have obtained an oil which they believe to consist of the second stilbene; this product yields the α-dibromide when treated with the halogen in ether. M. O. F.

Phenyl Derivatives of Ethane and Ethylene. By HEINRICH BILTZ (*Annalen*, 1897, **296**, 219—260. Compare Abstr., 1893, i, 718). —The author has shown (*loc. cit.*) that the action of aluminium chloride on benzene and chloral in carbon bisulphide gives rise to tetraphenylethane, tetraphenylethylene, triphenylvinylic alcohol, and diphenyldichlorethylene. The present paper describes the further investigation of these substances and their derivatives.

Tetraphenylethane, $CHPh_2\cdot CHPh_2$, crystallises from glacial acetic acid in long, colourless, prismatic needles, and melts at 207·5° (uncorr.), or at 211° when a short thermometer is used; it boils at 358—362°

(uncorr.), or at 379—383° (corr.). The hydrocarbon resembles in every particular the product obtained by Anschütz from stilbene dibromide.

Tetraparanitrotetraphenylethane, $C_2H_2(C_6H_4\cdot NO_2)_4$, is prepared by dissolving the finely powdered hydrocarbon in 20 parts of fuming nitric acid at 30—40°; the product is insoluble in alcohol, but crystallises from aniline in orange rhombohedra containing 4 mols. of the base. If the concentrated solution in aniline is cooled rapidly, colourless, monoclinic needles separate, consisting solely of the nitro-compound, which passes into the rhombohedral form when kept for some days in the mother liquor; the substance crystallises from nitrobenzene in prisms, and melts and decomposes at 300° (uncorr.), or at 337·5—338·5° (corr.). Tetranitrotetraphenylethane is indifferent towards concentrated sulphuric acid or an acetic acid solution of chromic acid, even resisting the action of fuming nitric acid at 110°; when chromic acid is added to a solution of the substance in concentrated sulphuric acid at 50°, however, paradinitrobenzophenone is produced.

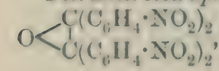
Tetraparamidotetraphenylethane, $C_2H_2(C_6H_4\cdot NH_2)_4$, obtained by reducing the nitro-derivative with tin and hydrochloric acid, crystallises in brown, monoclinic prisms; it melts at 264° (uncorr.), or at 272° when a short thermometer is employed. The *stannichloride* crystallises from water in small, lustrous needles, and the *acetyl* derivative separates from dilute acetic acid in colourless crystals melting at 336—337° (corr.); the base is readily diazotised, and the product yields colouring matters with phenols and amines.

Tetraphenylethylene crystallises from benzene after addition of alcohol in thin, highly refractive plates, and melts at 221° (uncorr.), or at 223·5—224·5° when a short thermometer is used; it does not form an additive compound with bromine, but yields a substitution product instead.

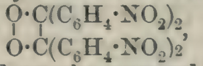
Tetraparabromotetraphenylethylene, $C_2(C_6H_4Br)_4$, is obtained on adding bromine to a solution of tetraphenylethylene in carbon tetrachloride, hydrogen bromide being evolved; it crystallises in long needles from carbon tetrachloride containing a small quantity of alcohol. The substance dissolves very readily in benzene, but more sparingly in carbon tetrachloride or glacial acetic acid, and is insoluble in alcohol; it melts at 248—249° (uncorr.), or at 253—255° on a short thermometer. Oxidation with chromic acid dissolved in glacial acetic acid converts the bromo-derivative into dibromobenzophenone (m. p. 175°).

Tetranitrotetraphenylethylene, $C_2(C_6H_4\cdot NO_2)_4$, is obtained by dissolving the hydrocarbon in concentrated nitric acid below 5°; it dissolves very readily in benzene and in nitrobenzene, and has not been crystallised, the amorphous compound melting at about 100°. Oxidation of the nitro-derivative gives rise to two products, according to the conditions under which the operation is conducted.

Tetranitrotetraphenylethylene oxide (*Tetranitro-α-benzopinacolin*),



$O<\begin{matrix}C(C_6H_4\cdot NO_2)_2\\ |\\ C(C_6H_4\cdot NO_2)_2\end{matrix}$, is prepared by adding chromic acid to a solution of the nitro-derivative in glacial acetic acid at 90°, and maintaining the temperature of the liquid at 80° during 4 hours; it dissolves sparingly in boiling glacial acetic acid, and crystallises from this solvent in colourless, triclinic needles. It melts at 294° (uncorr.), and at 298—299° on a short thermometer. It is not identical with *tetranitro-β-benzopinacolin*, $C_{26}H_{16}N_4O_9$, obtained on nitrating α- and β-benzopinacolins; the amorphous substance sinters at 120—140°, and has not been crystallised. Alcoholic potash develops a deep violet coloration, which ultimately becomes brownish.

Tetranitrotetraphenylethylene dioxide, 

$$\begin{array}{l} O\cdot C(C_6H_4\cdot NO_2)_2 \\ | \quad | \\ O\cdot C(C_6H_4\cdot NO_2)_2 \end{array}$$

is obtained from the mother liquor of the oxide, and may be prepared by oxidising tetranitrotetraphenylethylene with chromic acid in glacial acetic acid at 115—130°; it crystallises from glacial acetic acid in pale yellow, lustrous scales, and melts and decomposes at 183° (uncorr.). It is decomposed by concentrated sulphuric acid, which forms a deep yellow solution. The dioxide is somewhat soluble in fused naphthalene, but does not dissolve in boiling benzene.

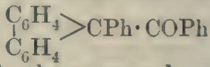
Diphenyldichlorethylene, $CPh_2\colon CCl_2$, crystallises from benzene in flattened plates, consisting of aggregates of lamellæ; it melts at 80°, and boils at 315° (uncorr.), or at 336° (corr.). The solution in warm concentrated sulphuric acid is yellow, becoming dark green on further heating, this colour changing to violet black and brownish-red as the temperature approaches the boiling point of the acid. The substance gives rise to additive compounds with bromine and chlorine.

Triphenylvinylic alcohol, $CPh_2\colon CPh\cdot OH$, crystallises from alcohol in lustrous, monoclinic plates, and melts at 136° (uncorr.); oxidation with an alkaline solution of potassium permanganate gives rise to benzophenone and benzoic acid, the same products being obtained with an acetic acid solution of chromic acid. Hydrolysis with alcoholic potash resolves the alcohol into diphenylmethane and benzoic acid. The *acetyl* derivative crystallises from dilute acetic acid in monoclinic prisms, and melts at 104·5—105·5°; attempts to prepare a benzoyl derivative by the Baumann-Schotten method and by Deninger's modification were, however, fruitless.

Tribromophenyltribromethane, $C_2Br_3(C_6H_4Br)_3$, obtained by the direct action of bromine on the alcohol, crystallises from benzene in slender needles melting at 245° (corr.). A simple additive compound of triphenylvinylic alcohol with bromine has not been obtained.

Triphenylethane, $CHPh_2\cdot CH_2Ph$, is prepared by reducing triphenylvinylic alcohol with hydriodic acid and phosphorus at 180°; it crystallises in colourless leaflets, and melts at 53·5—54·5°. A compound obtained from benzene, chlorodiphenylethane, and aluminium chloride has been described by Waas (Abstr., 1882, 1209) as having this constitution; it is, however, an oil which boils above 360°.

Phenylbenzoin ethyl ether, $COPh\cdot CPh_2\cdot OEt$, is obtained by heating triphenylvinylic alcohol with an alcoholic solution of hydroxylamine hydrochloride in a reflux apparatus, ammonium chloride being also produced; it crystallises in colourless, rhombic prisms. Alcoholic soda resolves the substance into benzhydrol ethyl ether, $CHPh_2\cdot OEt$, and benzoic acid.

The portion of the crude product from chloral and benzene which boils at 400°, crystallises immediately in the receiver; it melts at 233° (uncorr.), and appears to be identical with the hydrocarbon, $C_{26}H_{18}$ (possibly phenylbenzyldiphenylenemethane), obtained by Hanriot and St. Pierre by reducing a substance prepared from benzoic chloride and the potassium derivative of triphenylmethane (Abstr., 1889, 882). Oxidation with chromic acid in glacial acetic acid converts it into the compound,  $\begin{matrix}C_6H_4\\|\\C_6H_4\end{matrix}\!\!>CPh\cdot COPh$ (m. p. 172°), obtained by Hanriot and St. Pierre in the manner described.

The mother liquors accumulated during the investigation of the products from chloral, benzene, and aluminium chloride, were found to contain phenyldichlorethylene, diphenylmethane, triphenylmethane, and a very small quantity of benzoic acid. M. O. F.

Sulphoketones of the Naphthalene Series. By **Julius Troeger** and **F. Bolm** (*J. pr. Chem.*, 1897, [ii], **55**, 398—416).—By heating chloracetone, $CH_3\cdot CO\cdot CH_2Cl$, with a naphthalenesulphinate, $C_{10}H_7\cdot SO_2M$, in aqueous alcoholic solution, a naphthylsulphonacetone,

$$CH_3\cdot CO\cdot CH_2\cdot SO_2\cdot C_{10}H_7,$$

is obtained; this can be brominated in acetic acid solution, and then yields a naphthylsulphobromacetone, $CH_2Br\cdot CO\cdot CH_2\cdot SO_2\cdot C_{10}H_7$, which will react with a sulphinate, $R\cdot SO_2M$, yielding a disulphone,

$$R\cdot SO_2\cdot CH_2\cdot CO\cdot CH_2\cdot SO_2\cdot C_{10}H_7.$$

Compounds of this last type exhibit the distinctive ketonic reactions in a much less degree than usual; often they only react with hydroxylamine or phenylhydrazine when heated with these substances under pressure. β-Naphthyl derivatives are much more easily prepared than the isomeric α-compounds, as the latter crystallise with difficulty; of the disulphones, the naphthyl-tolyl one was most readily obtained.

β-Naphthylsulphonacetone melts at 130°; the yield was 80 per cent. of the theoretical. Its *oxime* melts at 172°, the yellowish *phenylhydrazone* at 147°; when it is mixed with thiophenol, a little benzene and powdered zinc chloride added, and dry hydrogen chloride passed in, *β-naphthylsulphonacetonephenylmercaptol*, $CH_3\cdot C(SPh)_2\cdot CH_2\cdot SO_2\cdot C_{10}H_7$, melting at 100°, is formed; when its alcoholic solution is saturated with gaseous ammonia, *β-naphthylsulphonacetonamine*,

$$CH_3\cdot C(NH)\cdot CH_2\cdot SO_2\cdot C_{10}H_7,$$

melting at 124°, is formed; with hydrogen cyanide and with sodium hydrogen sulphite, no compounds are formed. *β-Naphthylsulphomonobromacetone* melts at 130—132°; a *dibromo*-compound melting at 155—157° can also be obtained, and it appears that a tetrabromo-derivative is formed as a result of heating on the water bath with excess of bromine in acetic acid solution. *Di-β-naphthylsulphonacetone*, $CO(CH_2\cdot SO_2\cdot C_{10}H_7)_2$, melts at 200°, and forms an *oxime* melting at 116°. *β naphthylparatolylsulphonacetone*,

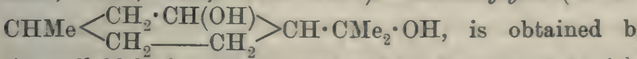
$$C_7H_7\cdot SO_2\cdot CH_2\cdot CO\cdot CH_2\cdot SO_2\cdot C_{10}H_{17},$$

melts and decomposes at 185°; the *oxime* melts at 158°, the yellow *phenylhydrazone* at 186°, and the *acetonamine* at 126°. *β-Naphthylphenylsulphonacetone*, $C_6H_5\cdot SO_2\cdot CH_2\cdot CO\cdot CH_2\cdot SO_2\cdot C_{10}H_7$, melts at 144°, the *oxime* at 167°, and the yellowish *phenylhydrazone* at 175°.

By acting on β-naphthylsulphomonobromacetone with sodium phenyl or sodium β-naphthyl sulphides, C_6H_5SNa, &c., *thiophenyl-* and *β-thionaphthyl-β-naphthylsulphonacetones* are obtained,

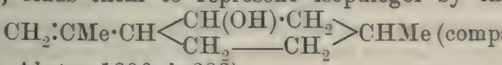
$$C_6H_5\cdot S\cdot CH_2\cdot CO\cdot CH_2\cdot SO_2\cdot C_{10}H_7,$$

&c.; by hot permanganate solution, these are oxidised to the corresponding disulphones. *α-Naphthylsulphonacetone* melts at 65°, and yields an *oxime*; both substances crystallise with difficulty. C. F. B.

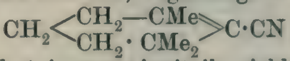
A Menthoglycol. By Philippe Barbier and Georges Leser (*Compt. rend.*, 1897, **124**, 1308—1311).—*Menthoglycol* (*menthanediol*-3 : 8),  $CHMe\left<\begin{matrix}CH_2\cdot CH(OH)\\ CH_2\text{———}CH_2\end{matrix}\right>CH\cdot CMe_2\cdot OH$, is obtained by agitating citronellaldehyde with 10 parts of 5 per cent. sulphuric acid during 12 hours; it is colourless, and almost odourless, crystallising from light petroleum in lustrous, white plates, melting at 81—81·5°. Acetic anhydride at 100° converts it into the *monacetyl* derivative, which boils at 137—138° under a pressure of 10 mm.; at 150°, in presence of fused sodium acetate, the anhydride gives rise to the acetyl derivative of isopulegol. Hydrogen chloride in presence of glacial acetic acid converts the glycol into what appears to be a mixture of two isomerides; the product has the formula $C_{10}H_{18}Cl\cdot OAc$, and boils at 124—125° under a pressure of 10 mm. The relation which the glycol bears to isopulegol is shown by the conversion of the latter into menthoglycol, and also by the fact that isopulegol is another product of the action of sulphuric acid on citronellaldehyde. A third *compound*, having the formula $C_{20}H_{34}O$, has been also isolated from the products of this action; it boils at 185° under a pressure of 10 mm.

The authors ascribe to citronellaldehyde the constitution

$$CH_2\colon CMe\cdot CH_2\cdot CH_2\cdot CH_2\cdot CHMe\cdot CH_2\cdot COH$$

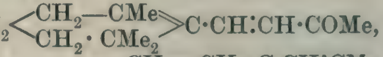
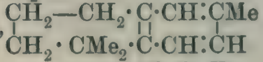
(compare Barbier and Bouveault, Abstr., 1896, i, 492). This view, however, leads them to represent isopulegol by the constitutional formula  $CH_2\colon CMe\cdot CH\left<\begin{matrix}CH(OH)\cdot CH_2\\ CH_2\text{———}CH_2\end{matrix}\right>CHMe$ (compare Tiemann and Schmidt, Abstr., 1896, i, 383). M. O. F.

Compounds of the *iso*-Geranaldehyde (*iso*-Citral) Series: Preparation and Constitution of Ionone. By Philippe Barbier and Louis Bouveault (*Bull. Soc. Chim.*, 1897, [iii], 15, 1002—1008). Compare Abstr., 1894, i, 83).—In attempting to prepare *iso*-geranionitrile according to the instructions of Tiemann and Semmler (*loc. cit.*), the authors have obtained the *hydrate*, $C_{10}H_{15}N,H_2O$, a viscous liquid which boils at 152° under a pressure of 10 mm.; it is not an amide, being converted into *iso*-geranionitrile under the influence of 70 per cent. sulphuric acid at 100°, the nitrile obtained in this way boiling at 97° under a pressure of 10 mm. (compare *loc. cit.*). *iso*-Geranionitrile is prepared by carefully adding geranionitrile to well cooled 70 per cent. sulphuric acid; another *hydrate* of *iso*-geranionitrile can also be formed, being produced by the action of hot, moderately concentrated sulphuric acid on *iso*-geranionitrile, and this compound separates from benzene in colourless crystals melting at 115°. *iso*-Geranionitrile resists the action of alcoholic potash at 100°, and to some extent also when heated with it at 170° under pressure, but a considerable portion under these conditions yields the *amide*, $C_9H_{15}\cdot CONH_2$, boiling at 208°, under a pressure of 10 mm., and melting at 121°, along with an isomeric *amide* which melts and sublimes at 202°; these compounds, although yielding nitrogen when treated with nitrous acid, have not been yet converted into *iso*-geranic acid.

The authors represent the constitution of geranionitrile and the hydrate by the expression $CMe_2{:}CH\cdot CH_2\cdot CH_2\cdot CMe{:}CH\cdot CN$ (compare *loc. cit.*), and $OH\cdot CMe_2\cdot CH_2\cdot CH_2\cdot CH_2\cdot CMe{:}CH\cdot CN$, regarding *iso*-geranionitrile as having the constitution  $CH_2{<}\begin{matrix}CH_2—CMe\\CH_2\cdot CMe_2\end{matrix}{>}C\cdot CN$; this conclusion is based on the observation that *iso*-geranionitrile yields hydrogen cyanide, acetone, *aa*-dimethylglutaric acid, and *aa*-dimethylsuccinic acid on oxidation.

Ionone is probably a compound of the *iso*-geranaldehyde series, being easily prepared by the action of sulphuric acid on ψ-ionone, the latter substance being produced from geranaldehyde by condensation with acetone (Tiemann and Krüger, Abstr., 1894, i, 82). ψ-Ionone is accordingly represented by the formula

$$CMe_2{:}CH\cdot CH_2\cdot CH_2\cdot CMe{:}CH\cdot CH{:}CH\cdot COMe,$$

ring formation yielding ionone,  $CH_2{<}\begin{matrix}CH_2—CMe\\CH_2\cdot CMe_2\end{matrix}{>}C\cdot CH{:}CH\cdot COMe$, which is transformed on dehydration into ionene,  $\begin{matrix}CH_2—CH_2\cdot C\cdot CH{:}CMe\\ | \qquad\qquad\quad \| \qquad\quad |\\ CH_2\cdot CMe_2\cdot C\cdot CH{:}CH\end{matrix}$ (compare Tiemann and Krüger, *loc. cit.*).

M. O. F.

Isolauronolic Acid. By G. Blanc (*Compt. rend.*, 1897, **124**, 1361—1364).—*iso*-Lauronolic acid dissolves readily in concentrated sulphuric acid, and on warming the solution on the water bath, is converted into sulphocamphylic acid (compare Abstr., 1893, i, 363); Koenigs and Hoerlin (*loc. cit.*) have obtained *iso*-lauronolic acid by the action of superheated steam on sulphocamphylic acid, and the author has prepared it by the action of aluminium chloride on camphoric anhydride (this vol., i, 201). It is noteworthy that, although *iso*-lauronolic acid is unsaturated, the sulphonic derivative has the properties of a saturated compound.

When the chloride of *iso*-lauronolic acid is heated with the sodium derivative of ethylic malonate suspended in toluene, the *compound*, $C_8H_{13}\cdot CO\cdot CH_2\cdot COOEt$, is produced; it is a mobile liquid, of agreeable odour, and boils at 185—190° under a pressure of 17 mm. The substance is very unstable, and an aqueous solution of caustic potash converts it into a gelatinous *compound* which is rapidly converted into potassium *iso*-lauronolate.

iso-*Lauronolylic cyanide*, $C_8H_{13}\cdot CO\cdot CN$, is obtained by heating dry silver cyanide with *iso*-lauronolylic chloride in sealed tubes at 100° during 4 hours; it is a mobile liquid, of penetrating odour, and boils at 120° under a pressure of 23 mm. Hydrolysis regenerates *iso*-lauronolic acid.

iso-*Lauronolonitrile*, $C_8H_{13}\cdot CN$, is formed as a bye-product in preparing the amide if considerable quantities of the acid chloride in ethereal solution are treated with gaseous ammonia, but it is more convenient to dehydrate the amide (this vol., i, 201) with acetic chloride or phosphorus pentachloride. It is a colourless, mobile liquid, of penetrating odour, and boils at 205° under a pressure of 760 mm.; reduction converts it into a base which will be described subsequently.

M. O. F.

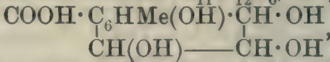
Cochineal Dye. By Carl T. Liebermann and Hugo Voswinckel (*Ber.*, 1897, **30**, 1731—1744. Compare this vol., i, 292).—The authors have shown that the colouring matter of cochineal, when oxidised with potassium persulphate, yields two acids, which they term coccinic and cochinelic acids, provisionally ascribing to these substances the formulæ $C_9H_8O_5$, and $C_{10}H_8O_7$ respectively (*loc. cit.*). Further investigation has established the identity of the former with hydroxyuvitic acid, which most probably has the constitution $OH\cdot C_6H_2Me(COOH)_2$ [$Me : OH : (COOH)_2 = 1 : 3 : 4 : 6$]; moreover, by the action of heat, water and carbonic anhydride have been eliminated from cochinelic acid, which thus gives rise to the anhydride of *β-coccinic acid*, an acid isomeric with hydroxyuvitic acid, having the constitution $OH\cdot C_6H_2Me(COOH)_2$ [$Me : OH : (COOH)_2 = 1 : 3 : 5 : 6$]. These observations, coupled with the fact that tribromocresotic acid, the product of brominating cochinelic acid, yields the cresotic acid melting at 210° when reduced, point to the formula $OH\cdot C_6HMe(COOH)_3$ [$Me : OH : (COOH)_3 = 1 : 3 : 4 : 5 : 6$] for cochinelic acid, which must be therefore regarded as a homohydroxyhemimellitic acid.

Silver cochinelate, containing $1H_2O$, is not insoluble in water, and remains hydrated when heated for some time at 75°. The calcium salt (*loc. cit.*) crystallises in small needles, and retains $7H_2O$ after being dried at 130°, but becomes anhydrous at 180°. The *barium* salt also forms needles, contains $2H_2O$ at 130°, and becomes anhydrous at 180°. The *methylic* salt, obtained from methylic iodide and the silver salt, melts at 78—80°; in agreement with Victor Meyer's generalisation regarding the etherification of the tricarboxylic acids, cochinelic acid, which contains carboxylic groups attached to three neighbouring carbon atoms, does not yield alkylic salts when treated with hydrogen chloride in presence of an alcohol. The *ethylic* salt is a viscous oil, which slowly dissolves in cold, dilute, caustic alkali, acids precipitating the *hydrogen diethylic* salt from the solution; this substance crystallises in colourless needles and scales resembling benzoic acid, and melts at 136—137°. The *acetyl* derivative crystallises from benzene and petroleum in plates, and melts indefinitely at 142—143°.

Tribromocresotic acid develops a yellow, and not reddish-violet coloration with ferric chloride (compare *loc. cit.*); when reduced with sodium amalgam, it yields cresotic acid melting at 210°, passage of carbonic anhydride accelerating the action, and giving rise to a colourless, resinous substance. Cresotic acid is also formed when cochinelic acid is heated with water in sealed tubes at 200—210° for 2—3 hours; if the operation is conducted at 170°, and interrupted after one hour, *a*-coccinic (hydroxyuvitic) acid is produced.

β-Coccinic acid, $OH\cdot C_6H_2Me(COOH)_2$ [$Me:OH:(COOH)_2 = 1 : 3 : 5 : 6$], is very readily soluble in water, and melts at 155—157°; ferric chloride develops a yellowish turbidity, but no red coloration, and the acid gives the fluorescein reaction when fused with resorcinol. The *anhydride* is obtained by heating cochinelic acid at 250—260° until gas is no longer evolved; it separates from benzene in small nodules, and melts at 166—168°. The *silver* salt is anhydrous.

The authors discuss the constitution of cochineal-carmine, and point out that this substance, which has the formula $C_{11}H_{12}O_6$, may prove to be the hydrindene derivative,



$$\begin{array}{l} COOH\cdot \underset{|}{C_6}HMe(OH)\cdot \underset{|}{C}H\cdot OH \\ \quad\quad\quad\;\; CH(OH)\text{——}CH\cdot OH \end{array}$$

, or the corresponding derivative of bis-hydrindene, $C_{22}N_{22}O_{12}$ (compare v. Miller and Rohde, Abstr., 1894, i, 94; also Schunck and Marchlewski, Abstr., 1895, i, 67). M. O. F.

Carminic Acid. By Wilhelm von Miller and Georg Rohde (*Ber.*, 1897, **30**, 1759—1766. Compare Abstr., 1894, i, 94; also Schunck and Marchlewski, Abstr., 1895, i, 67).—Carminic acid has been hitherto regarded by the authors as having the constitution of a hexahydroxy-α-methylnaphthalene, but the recognition of a carboxyl group compels them now to modify this view. The empirical formula of the compound is once more thrown in doubt, because the molecular weight is probably that of a substance having the composition $C_{24}H_{22}O_{14}$, or $C_{22}H_{20}O_{13}$ (compare preceding abstract).

The *acetyl* derivative, $C_{24}H_{12}O_{13}Ac_8$(?), is obtained by heating carminic acid with acetic anhydride (10 parts) and a small quantity of zinc chloride or concentrated sulphuric acid until dissolution is complete, the reddish-yellow liquid becoming brownish-red; on pouring the liquid into water, a bluish-yellow precipitate is formed. This is a mixture of acetyl derivatives, and is immediately hydrolysed to carminic acid when treated with cold dilute caustic alkali. The main product crystallises from methylic alcohol in long, bright yellow needles, and melts gradually at 155—165°, whilst the bye-product, which yields the foregoing substance on further acetylation, forms golden-yellow, microscopic needles, and melts, decomposing, at 210°; the latter *compound* gives analytical results which agree with the formula $C_{24}H_{16}O_{14}Ac_6$. It is the discovery that the acetyl derivative is a carboxylic acid which has led the authors to modify their views in the above-mentioned manner.

Carminic acid, in addition to the anilide described by Schunck and Marchlewski (*loc. cit.*), yields an additive *compound*,

$$(C_{12}H_{11}O_7)_2,C_6H_5\cdot NH_2,$$

which crystallises from 50 per cent. alcohol in red needles, and melts and decomposes at 190°. The quinoline additive *compound*,

$$(C_{12}H_{11}O_7)_2,C_9H_7N,$$

forms red scales, and melts and decomposes at about 220°.

M. O. F.

Metallic Compounds of Pyridine and the Electrolysis of Pyridine. By Ludwig Pincussohn (*Zeit. anorg. Chem.*, 1897, **14**, 379—403).—The paper contains an account of the metallic compounds of pyridine already described.

Lead chloride pyridine, $4PbCl_2,3C_5NH_5$, is obtained by dissolving lead chloride in boiling pyridine. It crystallises in white needles, deliquesces in the air and gives off a strong odour of pyridine. *Lead* *nitrate pyridine*, $Pb(NO_3)_2,2C_5NH_5$ and *lead iodide pyridine* are prepared in a similar manner and have similar properties.

Lead chloride pyridine hydrochloride, $2PbCl_2,C_5NH_5,HCl + 2H_2O$, is obtained by saturating an aqueous solution of pyridine hydrochloride with lead chloride and allowing the mixture to crystallise. It crystallises in slender, lustrous, white needles which are quite stable on exposure to the air. The author was unable to obtain the salt,

$$3PbCl_2,4C_5NH_5,HCl,$$

described by Classen and Zahorsky. The salts with *ferric chloride*, $Fe_2Cl_6,3C_5NH_5,HCl + 3H_2O$; *barium chloride*, $(BaCl_2)_3,C_5NH_5,HCl + H_2O$; *magnesium chloride*, and *silver chloride* are also described. With manganous chloride, two salts are obtained. The *salt*, $MnCl_2,2C_5NH_5,HCl$, is formed by saturating an aqueous solution of pyridine hydrochloride with manganous chloride and allowing the solution to crystallise; it separates in yellow crystals, melts at 170—175°, cannot be recrystallised without decomposition, and dissolves to a rose coloured solution in water and alcohol. The *salt*, $MnCl_2,C_5NH_5,HCl$, is obtained by dissolving molecular proportions of pyridine hydrochloride and manganous chloride in water and evaporating the solution on the water bath; it is deposited from alcohol in rose coloured crystals, and can be recrystallised without decomposition.

Silver nitrate pyridine nitrate, $5AgNO_3,3C_5NH_5,HNO_3$, is obtained by evaporating an aqueous solution of silver nitrate and pyridine nitrate on the water bath. It crystallises from alcohol in beautiful, silky needles, is stable on exposure to the air, and when heated in a porcelain crucible gives a beautiful silver mirror. The following nitrates are also described: with *uranium nitrate*, $UrO_2(NO_3)_2,3C_5NH_5,HNO_3 + 2H_2O$; with *copper nitrate*; with *lead nitrate*, $Pb(NO_3)_2,C_5NH_5,HNO_3$; with *cobalt nitrate*, $Co(NO_3)_2,3C_5NH_5,HNO_3$; with *strontium nitrate*, $Sr(NO_3)_2,C_5NH_5,HNO_3$.

The following *sulphates* are also described: *nickel sulphate pyridine sulphate*, $3NiSO_4,2C_5NH_5,H_2SO_4 + 10H_2O$, and the salts of pyridine sulphate with cobalt sulphate, $4CoSO_4,C_5NH_5,H_2SO_4 + 10H_2O$; with zinc sulphate, $3ZnSO_4,2C_2NH_5,H_2SO_4 + 2H_2O$; with ferrous sulphate, $8FeSO_4,C_5NH_5,H_2SO_4 + 3H_2O$; with aluminium sulphate,

$$Al_2(SO_4)_3,4C_5NH_5,H_2SO_4 + 6H_2O,$$

and with copper sulphate, $3CuSO_4,C_5NH_5,H_2SO_4 + 18H_2O$. Double salts with lead sulphate and with barium sulphate could not be obtained. Nearly all the above salts crystallise well, are stable on exposure to the air, and have no odour; whereas the compounds of pyridine with a metallic salt are very unstable and easily lose their pyridine, or the greater part of it, on exposure to the air. The latter salts can also be prepared by dissolving a metallic oxide in an aqueous solution of a pyridine salt, that is, pyridine hydrochloride. Lead chloride pyridine and lead nitrate pyridine have been prepared by this method.

Pyridine phosphate, $C_5NH_5,2H_3PO_4 + H_2O$, is obtained by neutralising phosphoric acid with pyridine, evaporating the mixture to a syrup, and allowing it to remain for some time. It is a white, amorphous mass, cannot be obtained crystalline, has no odour of pyridine, and is fairly stable on exposure to the air.

Pyridine tungstate, $C_5NH_5,2WO_2(OH)_2$, is obtained by mixing aqueous solutions of pyridine sulphate and sodium tungstate. It separates from hot water in microscopic crystals. *Pyridine molybdate*, $C_5NH_5,3MoO_2(OH)_2$, is obtained as a white precipitate by mixing solutions of pyridine sulphate and sodium molybdate. It is easily soluble in hot water, sparingly so in cold water.

The author is unable to confirm the results obtained by Ahrens (this vol., i, 368) in the electrolysis of pyridine. Piperidine is formed under some conditions in very small quantity only, but usually not at all, whereas Ahrens obtained 95 per cent. of the theoretical yield. The brown compound mentioned by Ahrens as being produced at the cathode in two only of his experiments, was obtained by the author in all cases except where a very small current density was employed. A *new base* of the composition C_5NH_7O is also formed at the cathode. It is insoluble in water, alcohol, ether, benzene, chloroform, and pyridine, soluble in a hot solution of pyridine sulphate, and in hot concentrated acids. The hydrochloride yields characteristic double salts with platinic chloride, picric acid, mercuric chloride, and potassium ferrocyanide. E. C. R.

Compounds of Pyridine, Piperidine and Quinoline with Metallic Salts. By RAOUL VARET (*Compt. rend.*, 1897, **124**, 1155—1157).—The general method of preparing the compounds described by the author is to dissolve the metallic salt in hot pyridine, filter out of contact with air, and allow to cool. Cuprous bromide yields green crystals of the composition $Cu_2Br_2,4C_5NH_5$; zinc iodide yields slender, prismatic needles of the compound $ZnI_2,2C_5NH_5$; zinc cyanide yields a gelatinous mass, the composition of which oscillates between $Zn(CN)_2,2C_5NH_5$ and $2Zn(CN)_2,3C_5NH_5$; cadmium bromide at a low temperature yields the compound $CdBr_2,6C_5NH_5$, and when this is dissolved in hot pyridine, the compound $CdBr_2,2C_5NH_5$ separates in long prismatic needles as the liquid cools; nickel bromide yields green crystals of the compound $NiBr_2,2C_5NH_5$ in addition to the compound $NiBr_2,4C_5NH_5$, previously described.

All these compounds are very soluble in hot pyridine; when the crystals are heated pyridine is volatilised.

The author has also prepared compounds of pyridine, piperidine and quinoline with halogen salts of aluminium and iron, with barium, strontium, and calcium iodides, and with manganese bromide and iodide. He has also investigated the action of piperidine on zinc, cadmium, nickel, and cobalt chlorides, bromides, and iodides, and has prepared compounds of quinoline with salts of silver, mercury, copper, &c. These compounds will be described in a subsequent paper. C. H. B.

1-Methylpyrrolidine. By GIACOMO L. CIAMICIAN and ANTONIO PICCININI (*Ber.*, 1897, **30**, 1789—1791).—1-Methylpyrrolidine, obtained by reducing 1-methylpyrroline with hydriodic acid and phosphorus at 250°, appears to be identical in every particular with the base obtained from hygric acid by Liebermann and Cybulski (Abstr., 1895, i, 311). The picrate crystallises in golden-yellow scales, and melts at 218°; the aurochloride forms yellow needles and melts at 218—219°.

M. O. F.

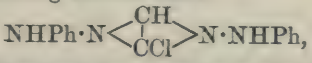
Action of Antipyrine on Trihydric Phenols. By GUSTAVE PATEIN and E. DUFAU (*Bull. Soc. Chim.*, 1897, [iii], **15**, 1048—1050. Compare this vol., i, 297 and 375).—*Pyrogallol-antipyrine*,

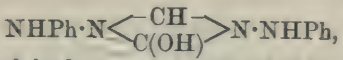
$$C_6H_3(OH)_3,C_{11}H_{12}N_2O,$$

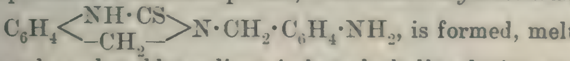
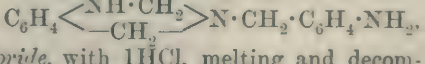
separates as an oil on mixing concentrated aqueous solutions of antipyrine and pyrogallol; it forms colourless crystals and melts at 77—78°. *Phloroglucinol-antipyrine* melts at 182—184°.

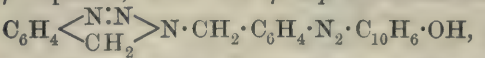
When aqueous solutions of antipyrine and gallic acid are mixed, an oil separates, and soon deposits crystals; the liquid, however, appears to be more in the nature of a solution than a compound, and no evidence of combination has been obtained. M. O. F.

Action of Chloral Hydrate on Phenylhydrazine: Diphenylglyoxazole and its Derivatives. By HENRI E. CAUSSE (*Compt. rend.*, 1897, **124**, 1029—1032).—*Trichlorethylidene-bisphenylhydrazine*, $CCl_3\cdot CH(NH\cdot NHPh)_2$, is a very unstable compound obtained on adding an aqueous solution of chloral hydrate to phenylhydrazine hydrochloride dissolved in water; it forms colourless crystals, but when exposed to air it immediately loses hydrogen chloride and becomes amorphous, ultimately resembling aniline black.

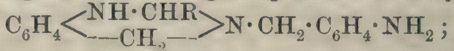
Chlorodiphenylglyoxazole,  $NHPh\cdot N<\begin{smallmatrix}CH\\ |\\ CCl\end{smallmatrix}>N\cdot NHPh$, is prepared by adding chloral hydrate dissolved in water to a solution of phenylhydrazine phosphate in aqueous glycerol (compare Causse, this vol., i, 408); it is a deep red, crystalline powder, insoluble in water, but dissolving in alcohol, ether, and chloroform. It readily loses chlorine under the influence of alkalis.

Hydroxydiphenylglyoxazole,  $NHPh\cdot N<\begin{smallmatrix}-CH-\\ C(OH)\end{smallmatrix}>N\cdot NHPh$, is obtained by the action of chloral hydrate on phenylhydrazine thiosulphate; it is an orange-coloured, crystalline powder, and melts at 146°. The *barium* derivative forms microscopic, yellow crystals, and the *antimony* derivative, prepared from chloral hydrate and antimony phenylhydrazine tartrate, is scarlet. M. O. F.

Orthamidobenzylamines. IV. By MAX BUSCH (*J. pr. Chem.*, 1897, [ii], **55**, 356—375.)—[With RUD. BIRK and WILHELM LEHMANN.]—*Diorthamidodibenzylamine*, $NH(CH_2\cdot C_6H_4\cdot NH_2)_2$, was prepared by reducing dinitrodibenzylamine (the *hydrochloride* of which melts and decomposes at 236°) with tin and hydrochloric acid; it melts at 71°, and forms a *hydrochloride* (with 3HCl) melting above 280°, and a *tribenzoyl* derivative melting at 218°. When it is heated with carbon bisulphide in the presence of alcoholic potash, *orthamidobenzylthiotetrahydroquinazoline*,  $C_6H_4<\begin{smallmatrix}NH\cdot CS\\ -CH_2-\end{smallmatrix}>N\cdot CH_2\cdot C_6H_4\cdot NH_2$, is formed, melting at 212°. This can be reduced by sodium, in hot alcoholic solution, to *3-orthamidobenzyltetrahydroquinazoline*,  $C_6H_4<\begin{smallmatrix}NH\cdot CH_2\\ -CH_2-\end{smallmatrix}>N\cdot CH_2\cdot C_6H_4\cdot NH_2$, (which forms a stable *hydrochloride*, with 1HCl, melting and decomposing at 280—300°, and a yellow *platinochloride* melting above 300°); by diazotisation and subsequent treatment with β-naphthol, it yields an orange-red azo-dye, *β-naphtholazobenzylthiotetrahydroquinazoline*, melting at 225°. When diamidodibenzylamine is itself diazotised (with 2 mols. of nitrous acid) and then treated with β-naphthol, dark red *β-naphtholorthazobenzyl-β-phenodihydrotriazine*,



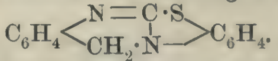
$C_6H_4<\substack{N{:}N\\ CH_2}>N\cdot CH_2\cdot C_6H_4\cdot N_2\cdot C_{10}H_6\cdot OH$, melting and decomposing at 185°, is formed. It condenses readily with aldehydes, $R\cdot COH$, at the ordinary temperature, forming compounds of the type



$$C_6H_4<\substack{NH\cdot CHR\\ CH_2}>N\cdot CH_2\cdot C_6H_4\cdot NH_2\ ;$$

benzaldehyde yields *2-phenyl-3-orthamidobenzyltetrahydroquinazoline* melting at 140°; salicylaldehyde and parahydroxybenzaldehyde yield the similar *2-orthohydroxyphenyl* and *2-parahydroxyphenyl* compounds, which melt at 166° and 90° respectively.

[With RUD. BIRK.]—When orthomethoxyphenylthiotetrahydroquinazoline is heated for 5 hours in a sealed tube at 140—145° with twenty times its weight of hydriodic acid (sp. gr. 1·96) and a little acetic acid, a substance is obtained that melts at 160—161°, and forms an orange *platinochloride* melting above 280°; it is doubtless a thiazole derivative,



$C_6H_4<\substack{N=C\cdot S\\ CH_2\cdot N}>C_6H_4$.

When orthamidobenzylamine derivatives of the type

$$NHR\cdot CH_2\cdot C_6H_4\cdot NH_2$$

are treated with 2 mols. of nitrous acid, compounds of the general formula $NO\cdot NR\cdot CH_2\cdot C_6H_4\cdot N{:}NCl$ are formed, which yield azo-dyes with β-naphthol in the usual manner. *Ortho-β-naphtholazobenzylphenylnitrosamine* is orange-red, melts at 155°, and exchanges the NO group for H when it is heated with alcoholic hydrochloric acid, yielding *β-naphtholazobenzylaniline*, which is red, with a yellow shimmer, and melts at about 176°. *β Naphtholazobenzylorthotolylnitrosamine* melts at 147—148°, and resembles the phenyl compound in colour and reactions.

C. F. B.

Solubility of Ecgonine. By WILLIAM OECHSNER DE CONINCK (*Compt. rend.*, 1897, **124**, 1159—1160).—The author has determined the solubility of ecgonine in the ordinary media; the results are stated in c.c. of the solvent required to dissolve 1 gram of the alkaloid. Distilled water, 4·6 at 17°; ethylic alcohol (95°), 67 at 17°; ethylic acetate, 77 at 20·6°; methylic alcohol ("rectified"), 18·5 at 19·2°; ethylic alcohol ("rectified") 17 at 19·6°; ethylic alcohol (71°), 21·3 at 19·8°; paraldehyde, 133·4 at 17·7°. The alkaloid is insoluble in the following media: ether, acetone, petroleum (b. p. 32—50° and b. p. 50—65°), chloroform, bromoform, benzene, toluene, isobutyric alcohol, ethylenic bromide, carbon bisulphide, carbon tetrachloride, and French turpentine.

M. O. F.

Organic Chemistry.

Action of Nickel on Ethylene: Synthesis of Ethane. By Paul Sabatier and Jean Baptiste Senderens (*Compt. rend.*, 1897, **124**, 1358—1361. Compare this volume, i, 305).—When ethylene is passed with moderate rapidity over nickel previously reduced in hydrogen, and heated at a temperature not exceeding 325°, the issuing gas is a mixture of about 10 volumes of hydrogen with about 60 volumes of ethane and 30 volumes of methane. At higher temperatures, the proportion of ethane diminishes, and only traces remain when the temperature approaches a dull red heat. It would seem that the first change is the decomposition of ethylene into carbon and ethane, the latter, at higher temperatures, being converted into carbon and methane, the methane ultimately splitting up into carbon and hydrogen. Direct experiments show that ethane is partially decomposed by nickel at 325°, and that pure methane is also decomposed, especially above 390°. A long column of nickel has practically the same effect on ethane as an increase of temperature, and even at 325° ethylene can be converted almost completely into methane, mixed with a small quantity of hydrogen.

In order to prepare ethane, a mixture of hydrogen with an excess of ethylene is passed over reduced nickel, heated at a temperature not exceeding 150°, and the process may go on for several hours with a comparatively small quantity of nickel. The process has, therefore, the advantage over Wilde's method, in which platinum is used but has to be continually renewed. Reduced cobalt, iron, or copper cannot be substituted for the nickel.

Under similar conditions, ethylene shows no tendency to combine with either water or ammonia. C. H. B.

Action of Acetylene on Silver Nitrate. By R. Chavastelon (*Compt. rend.*, 1897, **124**, 1364—1366).—When acetylene is passed into an aqueous solution of silver nitrate, a white precipitate is formed, and the acidity of the liquid increases somewhat rapidly until all the silver nitrate has been precipitated, and afterwards it increases slowly. In presence of an excess of the silver salt, the quantity of free nitric acid is always higher than that which corresponds with the quantity of silver nitrate that has disappeared. The acetylene compound combines with some silver nitrate as such, and the quantity of silver nitrate decomposed is twice as great as that which enters into combination in this way. Experiments with definite volumes of acetylene, combined with an analysis of the precipitate, show that the first compound formed has the composition $C_2Ag_2,AgNO_3$. It is decomposed by the prolonged action of acetylene, or by hot ammonia solution, the silver nitrate being decomposed or dissolved, whilst silver carbide, C_2Ag_2, is left. The action of acetylene on an ammoniacal solution of the silver salt yields silver carbide at once, as Keiser has stated. These results are analogous to those obtained by

Bruylants and Béhal with hydrocarbons derived from acetylene by substitution. C. H. B.

Compounds of Hydrocarbons with Metallic Salts. By KARL A. HOFMANN and F. KÜSPERT (*Zeit. anorg. Chem.*, 1897, **15**, 204—207).—The *compound*, $(Cu_2Cl_2)_3,C_2H_2$, obtained by the action of pure acetylene on a solution of anhydrous cupric chloride in absolute alcohol, crystallises in colourless needles; the same compound is obtained when methylic alcohol is employed, but the substance then crystallises in forms resembling those of Karlsbad feldspar. When treated with water, it is converted into copper acetylide, whilst with hydrochloric acid it is decomposed into acetylene and cuprous chloride. The reduction of the cupric chloride is due to the action of the acetylene, for by mixing the alcoholic filtrate from the crystals with water, and extracting the mixture with ether, an oily liquid is obtained which yields acetylene when treated with zinc. The compound is not explosive. If 75 per cent. alcohol is employed in the preparation, a reddish-brown powder is obtained which is slightly explosive, and, when treated with hydrochloric acid, yields acetylene, cuprous chloride, and a black residue.

The *compound*, $Ni(CN)_2,NH_3,C_6H_6$, which is formed in small quantities by the action of coal gas on a mixture of nickel hydroxide and ammonia, is easily obtained by shaking a solution of freshly-precipitated nickel cyanide in strong ammonia with benzene. It is a bluish-white powder; when heated, it becomes green, then brown, and finally black, and a very voluminous carbonaceous residue is formed, ammonium cyanide volatilising. Although, when boiled with water, or with a solution of potassium cyanide, the benzene is liberated, it is in very stable combination; no dissociation takes place when the compound is kept in a vacuum, and the benzene is only partially removed by prolonged washing with ether. E. C. R.

Aluminium Alkoxides. By HOMER WINTHROP HILLYER (*Amer. Chem. J.*, 1897, **19**, 597—603. Compare this vol., i, 235).—In the preparation of these substances, platinic chloride can be used, as well as mercuric and stannic chlorides; when stannic chloride is used, the absence of water is essential. Ferric, and even aluminium, chloride can be used, but, in these cases, heat is necessary in order to start the reaction. Finally, if a little alcoholic hydrogen chloride be added to alcohol standing over aluminium cuttings, a reaction will occur.

Aluminium methoxide and *isopropoxide* were prepared, but they crumbled to a dark powder when heated, and gave no distillate. *Aluminium propoxide* boils at 255° under 15 mm. pressure, and resembles commercial glucose in appearance. *Aluminium amyloxide* is yellow, and boils at 291° under 12 mm. pressure. Stannic chloride appears to have been used in the preparation of these substances. C. F. B.

Interaction of Glycerol and Acetic Acid. By ADOLF C. GEITEL (*J. pr. Chem.*, 1897, [ii], **55**, 417—429).—Triacetin is undoubtedly formed when glycerol is treated with acetic acid, the best method being to heat 200 grams of dry glycerol with 500 grams of acetic acid for

8 hours, and after distilling off the acetic acid under diminished pressure, to add 150 grams more of acid, and continue the heating for 16 hours longer. Triacetin, which is best isolated from the product by diluting with water and extracting with ether, is a colourless liquid, only slightly soluble in water, 100 c.c. of its aqueous solution saturated at 15° containing 7·17 grams of the compound. It has a sp. gr. = 1·1605 at 15°/15°, and distils without decomposition at 172—172·5° under a pressure of 40 mm.

On concentrating the aqueous solution left after extraction with ether, and fractionating the product under a pressure of 40 mm., diacetin passed over between 175—176°; it is a soluble, colourless liquid, having a sp. gr. = 1·1769 at 15°/15°.

In order to isolate the monacetin formed in the reaction, the aqueous solution, after the extraction of the triacetin, was extracted for 8 hours with ether at 34—35° in an extracting apparatus for liquids; the later extracts were collected separately, diluted with an equal volume of water, and, after being extracted with hot benzene, were concentrated. The monacetin was thus obtained as a thick, colourless liquid of sp. gr. = 1·2212 at 15°/15°.

By prolonging the ether extraction still further, *monacetyldiglycerol*, $C_3H_5(OH)_2\cdot O\cdot C_3H_5(OAc)\cdot OH$, was obtained. It is a colourless liquid having a sp. gr. = 1·2323 at 15°/15°; this compound is formed in larger quantities when the conditions of the experiment are such that the monacetin first formed remains in contact with the glycerol for some time. Diacetyldiglycide was also separated from the monacetin on fractionation; moreover, triacetyldiglycerol was obtained from the first ether extract, in the separation of the monacetin. J. F. T.

Molecular Volumes of Crystallised Carbohydrates. By JOSEPH PIONCHON (*Compt. rend.*, 1897, **124**, 1523—1524).—Playfair and Joule found that the molecular volumes of saccharose and lactose at 0° are identical with the volume of the water, as ice, of which they contain the elements. The author has determined the specific gravities at 0° of other carbohydrates with the following results:

Sugar.	Sp. gr. at 0°.	Molecular volume.	Volume of water as ice.	Difference between observed and calculated sp. gr.
Xylose	1·535	97·7	97·99	0·005
Glucose	1·538	117·0	117·6	0·008
Levulose	1·555	115·7	117·6	0·025
Saccharose	1·59	215·1	215·6	0·004
Lactose ($+H_2O$)	1·53	235·2	235·2	0·000
Melezitose ($+2H_2O$)	1·5565	347·7	352·8	0·026
Raffinose ($+5H_2O$)	1·465	405·4	411·58	0·022

Even where the divergence from the numbers required by Joule and Playfair's law is greatest, it does not amount to 2 per cent.

Adopting for carbon the volume 9·9, hydrogen 6·2, and oxygen 5·5, 2·3, or 0·4, according as it is acidic, alcoholic, or aldehydic, the formula for the volume of a solid carbohydrate, $C_\alpha H_\beta O_\gamma$, becomes

$$V_m = 9{\cdot}9\alpha + 6{\cdot}2\beta + 5{\cdot}5\gamma + 2{\cdot}3\gamma' + 0{\cdot}4\gamma'' + 24{\cdot}6,$$

and this agrees very closely with the observed values in the case of anhydrous carbohydrates. In the case of lactose, melezitose, or raffinose, which contain water of crystallisation, it is necessary to add a fourth value of the oxygen actually present as water, the latter being regarded as ice. When this is done, the observed and calculated values are practically identical. C. H. B.

The Glycogen of Fungi and Yeasts. By G. Clautriau (*Bied. Centr.*, 1897, **26**, 423—424; from *D. Bierbrauer.*, 1896, Heft. 9, 131).—Glycogen from animal and vegetable sources behaved analogously in all the experiments made. They are ternary, non-nitrogenous compounds, which are not in combination with any mineral substance. Their pseudo-solutions are precipitated by alcohol, acetic acid, and certain salts. They are all strongly dextrorotatory: D = 189·18°. The action of diastase or dilute acids on glycogens of different origin give rise to the same compounds.

Yeast-glycogen gives a brownish-violet coloration with iodine, whilst the other glycogens are coloured brownish-red. Whilst the latter become almost colourless at 58—60°, yeast-glycogen retains a brown tint at that temperature, but becomes colourless at 72—73°; on cooling, the colour returns.

Another slight difference observed between the various glycogens was their behaviour when dried; in one case, the glycogen was obtained in light flakes, in another case, in a compact condition. The opalescence of yeast-glycogen is less than that of the others.

The results do not decide whether there is only one glycogen. It is suggested that the slight differences observed may be due to polymerisation, or that there may be isomerides. N. H. J. M.

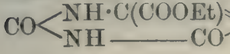
A Peculiarity of Soluble Starch. By Martinus Willem Beyerinck (*Bied. Centr.*, 1897, **26**, 430; from *Centr. Bakt.*, 1896, **2**, 697).—Soluble starch retains the properties and structure of starch grains, but dissolves in all proportions in boiling water, from which it separates, on cooling, in an amorphous form. The solutions cannot be mixed with gelatin solutions, but form an emulsion when shaken. With a 20 per cent. solution of starch and a 5 per cent. gelatin solution, a plate of starch is formed, with enclosed drops of gelatin; the latter in turn enclose extremely finely divided drops of starch. When the amount of gelatin is increased, so many gelatin drops are formed that they touch one another on solidifying, and flatten, so that artificial cell-tissues can be produced, the walls of which consist of starch, the contents being gelatin. With a still greater amount of gelatin, the starch separates as drops, which, however, do not show double refraction. If salt is added, a certain amount of starch dissolves in the gelatin. Glycerol (20 per cent. or more) seems to produce a complete solution.

When undisturbed, the specifically heavier starch solution effects a separation of the constituents. With gelatin or agar, with inulin, or gum arabic or dextrin, this was not observed, so that it seems to be a question of a specific property of the starch in relation to gelatin. The amount of water may be varied considerably without materially affecting the result. N. H. J. M.

Condensation of Guanidine and of Carbamide with Ethylic Oxalate. By R. Müller (*J. pr. Chem.*, **55**, 505—507).—Guanidine and ethylic oxalate yield *ethylic dioxalguanidine*,

$$NH{:}C[N{:}C(COOEt)\cdot CH_2\cdot COOEt]_2,$$

a substance which crystallises in plates melting at 147°. With carbamide, two substances can be obtained, the one when 2 mols. of the oxalate combine with 1 mol. of carbamide is *ethylic dioxalcarbamide*, $CO[N{:}C(COOEt)\cdot CH_2\cdot COOEt]_2$, crystallising in white prisms which melt at 104°, and the other when 1 mol. of the oxalate combines with 2 mols. of carbamide, the product being *ethylic uracilcarboxylate*,



$CO<\begin{matrix}NH\cdot C(COOEt)\\ NH\text{———}CO\end{matrix}>CH$, crystallising in needles and melting at 189°.

J. F. T.

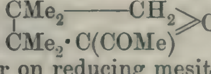
Behaviour of Chloral Hydrate with Ammonium Sulphide. By Joseph Lesinsky and Charles Gundlich (*Amer. Chem. J.*, 1897, **19**, 603—606).—When 2 grams of chloral hydrate are dissolved in 25 c.c. of water, and 10 c.c. of the solution rapidly mixed with 5 c.c. of yellow ammonium sulphide in a narrow beaker, after a certain lapse of time (which is always the same for the same temperature), a precipitate is suddenly formed. At 1°, 20°, 45°, and 65° respectively, the separation takes place after 44, 19, 8, and 3 seconds. The precipitate is pink to yellowish-brown, but its nature has not yet been determined. Butylchloral (crotonchloral) gives a similar reaction, but the precipitate is lemon-yellow, and is formed in 2 or 3 seconds. C. F. B.

Condensation Products of Isovaleraldehyde. By Albert Reychler (*Bull. Soc. Chim.*, 1896, [iii], **15**, 970—973).—Isovaleraldehyde was heated for several hours with dry potassium carbonate, and the product distilled under reduced pressure. After several fractionations, a substance was obtained boiling at 140—145° (20 mm.), and having the formula $C_{10}H_{20}O_2$; its sp. gr. at $22° = 0{\cdot}8962$, and its index of refraction at $22° = 1{\cdot}42995$. It reduces an ammoniacal solution of silver nitrate only after the addition of a caustic alkali, and does not react either with hydroxylamine or with phenylhydrazine. The author is studying the constitution of this substance.

From the higher fractions obtained in the distillation of the products of the action of chromic acid mixture on amylic alcohol, a fraction boiling at 137—141° (20 mm.) was obtained. The formula of this substance is $C_{15}H_{32}O_2$, its sp. gr. $= 0{\cdot}835$ at 22°, and its index of refraction $= 1{\cdot}42289$ at 22°. It is probably identical with the amylidenediamylic ether, $C_4H_9\cdot CH(O\cdot C_5H_{11})_2$, prepared by Alsberg.

A. C. C.

Reduction of $\alpha\beta$-Unsaturated Ketones. By Carl D. Harries and Friedrich Hübner (*Annalen*, 1897, **296**, 295—328).—Deoxymesitylic oxide (Δ^1-*cyclopentene-2-methyl-4-dimethyl-5-dimethyl-1-ethanone*),

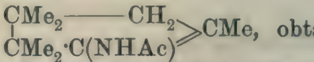


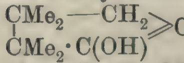
$\begin{matrix}CMe_2\text{———}CH_2\\ CMe_2\cdot C(COMe)\end{matrix}>CMe$, is the compound first obtained by von Baeyer on reducing mesitylic oxide, and subsequently investigated by Claisen (compare also Harries and Eschenbach, Abstr., 1896, i, 306, and Kerp, Abstr., 1896, i, 448). When the reduction is carried out by means of sodium amalgam, the portion of the product which boils at

210—230° yields two isomeric oximes, but only one derivative is obtained when aluminium amalgam is employed.

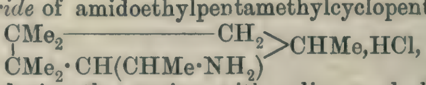
The *α-oxime* is the sole product of the action of hydroxylamine on the oil obtained by reducing mesitylic oxide with aluminium amalgam; it separates from alcohol in rhombic, hemimorphic crystals, and melts at 156—157°. The *hydrochloride* crystallises from alcohol in six-sided leaflets containing $1H_2O$, and melts at 124—125°.

The *β-oxime* is obtained along with the foregoing when the product of reduction of mesitylic oxide with sodium amalgam is treated with hydroxylamine; the substance also melts at 156—157°, but the crystals are of different habit, although belonging to the rhombic system. The *hydrochloride* melts at 105—106°.

Acetamidopentamethylcyclopentene,  $\left.\begin{array}{l}\mathrm{CMe_2}\text{———}\mathrm{CH_2}\\ \mathrm{CMe_2{\cdot}C(NHAc)}\end{array}\right>\mathrm{CMe}$, obtained by heating the oxime with concentrated mineral acid in a reflux apparatus, is a colourless oil which boils at 89—91° under a pressure of 10—12 mm. The *hydriodide* melts at 170°, and the *picrate* crystallises from alcohol in pale yellow, six-sided plates melting at 179—180°; the *aurochloride* and *platinochloride* are also crystalline.

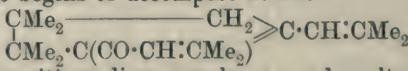
Pentamethyl-Δ^1-cyclopentenol,  $\left.\begin{array}{l}\mathrm{CMe_2}\text{——}\mathrm{CH_2}\\ \mathrm{CMe_2{\cdot}C(OH)}\end{array}\right>\mathrm{CMe}$, is a bye-product of the action of mineral acids on the oxime, and is isolated by submitting the product to distillation in a current of steam; it is a colourless, refractive oil, having the odour of camphor, and boils at 60—62° and 93—95° under pressures of 8 mm. and 34 mm. respectively. Oxidation with chromic acid in glacial acetic acid gives rise to tetramethylsuccinic acid.

The *hydrochloride* of amidoethylpentamethylcyclopentane,



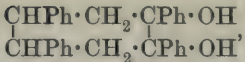
$$\left.\begin{array}{l}\mathrm{CMe_2}\text{——————}\mathrm{CH_2}\\ \mathrm{CMe_2{\cdot}CH(CHMe{\cdot}NH_2)}\end{array}\right>\mathrm{CHMe,HCl},$$

is obtained on reducing the α-oxime with sodium and absolute alcohol, and melts at 214—215°. The *hydrobromide* melts at 187—188°, and the *platinochloride* begins to decompose at 100°.

Deoxyphorone,  $\left.\begin{array}{l}\mathrm{CMe_2}\text{——————}\mathrm{CH_2}\\ \mathrm{CMe_2{\cdot}C(CO{\cdot}CH{:}CMe_2)}\end{array}\right>\mathrm{C{\cdot}CH{:}CMe_2}$, is prepared by reducing phorone with sodium amalgam, and melts at 108—109°; Claisen obtained it by means of zinc dust and sulphuric acid. The hydroxylamine *compound* crystallises in aggregates of needles and melts at 133—134°; the substance is not an oxime, and reduces Fehling's solution when moderately heated.

Deoxyphorone pinacone, $C_{36}H_{58}O_2$, prepared by heating deoxyphorone with zinc dust and sulphuric acid in a reflux apparatus, crystallises from benzene in needles, and melts at 194—195°. The solution in concentrated sulphuric acid is dark red.

The *compound*, $C_{15}H_{24}O$, is produced along with deoxyphorone, when phorone is reduced; it boils at 137—139° under a pressure of 8—10 mm.

The secondary *alcohol* of benzylacetophenone, $CH_2Ph{\cdot}CH_2{\cdot}CHPh{\cdot}OH$, is obtained on reducing benzylideneacetophenone in alcoholic solution with sodium amalgam; it boils at 330—332° under atmospheric pressure. The *compound*,  $\begin{array}{l}\mathrm{CHPh\cdot CH_2\cdot CPh\cdot OH}\\ \mathrm{CHPh\cdot CH_2\cdot CPh\cdot OH}\end{array}$, is produced under the same conditions, and after crystallisation from xylene melts at 210—211°; reduction with hydriodic acid and phosphorus in glacial acetic acid solution converts it into the *compound*, $C_{30}H_{28}O$, which sinters at 175° and melts at 182°.

It has been observed by Schneidewind that benzylacetophenone is the chief product of reducing benzylideneacetophenone with zinc dust and glacial acetic acid. The *compound* $C_{30}H_{26}O_2$ is produced along with it, and crystallises from xylene in slender needles melting at 270°.

M. O. F.

Action of Nitric Peroxide on Isonitrosoketones. By GIACOMO PONZIO (*Gazzetta*, 1897, **27**, i, 271—279).—Nitric peroxide acts on aliphatic isonitrosoketones of the composition $R\cdot CO\cdot C(NOH)R'$ much as nitric acid acts on ketones, with formation of diketones, dinitroketones, and varying proportions of dinitro-hydrocarbons and aliphatic acids. The first reaction which occurs is in accordance with the equation $2R\cdot CO\cdot C(NOH)R' + 2N_2O_4 = 2R\cdot CO\cdot C(NO_2)_2R' + N_2O + H_2O$; the dinitro-ketones thus formed are characterised, as has been shown by Fileti and Ponzio (Abstr., 1895, i, 499; this vol., i, 317), by hydrolysing in accordance with the equation $CMe(NO_2)_2\cdot CO\cdot CH_2\cdot CHMe_2 + H_2O = CHMe(NO_2)_2 + CHMe_2\cdot CH_2\cdot COOH$. Isonitrosoacetone, which, according to these equations, should yield acetyldinitromethane and methylglyoxal when treated with nitric peroxide, behaves exceptionally, and, without evolution of gas, gives a white, viscid mass, which inflames spontaneously when left, even in contact with water.

The general method of operating is to add the proper quantity of a dry ethereal solution of nitric peroxide to a cooled solution of the isonitrosoketone in anhydrous ether; the evolution of gas ceases after several hours, and the product is then washed with water, dried with sodium sulphate, and the ether distilled off, when a yellow oil is left. The oil thus obtained from isonitrosodiethylketone is washed with sodium hydrogen carbonate solution, which removes acetylpropionyl and dinitroethane; the residue consists of impure *propionyldinitroethane*, $CMe(NO_2)_2\cdot CO\cdot CH_2Me$, which crystallises in lustrous laminæ melting at 43—44°, is very volatile, and possesses a camphor-like odour. It is very readily hydrolysed by water, yielding propionic acid and dinitroethane.

Isonitrosoethyl isopropyl ketone, $CMe(NOH)\cdot CO\cdot CHMe_2$, which is easily prepared by Claisen and Manasse's method (Abstr., 1889, 584), crystallises in lustrous needles melting at 93—94°, and is very volatile in a current of steam. On treatment with hydroxylamine, it yields *acetylisobutyryldioxime*, $CMe(NOH)\cdot C(NOH)\cdot CHMe_2$, which crystallises in long needles melting at 155—156°. The oil obtained on treating the ketone with nitric peroxide solidifies slowly, depositing *isobutyryldinitroethane*, $CMe(NO_2)_2\cdot CO\cdot CHMe_2$, which crystallises in lustrous laminæ melting at 58°, and is also obtained on treating ethyl isopropyl ketone with nitric acid; the oil separated from the dinitro-compound contains acetylisobutyryl and dinitroethane.

Isonitrosoethyl isobutyl ketone, $CMe(NOH)\cdot CO\cdot CH_2\cdot CHMe_2$, prepared by treating ethyl isobutyl ketone with amylic nitrite, crystallises in flattened, lustrous needles melting at 64—65°; the *dioxime* obtained from it melts at 171—172°. *βa-Acetylisovalerylphenylhydrazoxime*,

$$CMe(NOH)\cdot C(N_2HPh)\cdot CH_2\cdot CHMe_2,$$

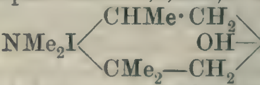
is prepared by heating the ketone with phenylhydrazine in alcoholic solution; it crystallises in almost colourless prisms melting at 127—128°, and on boiling its alcoholic solution with fuming hydrochloric acid yields *β-acetylisovalerylphenylhydrazone*,

$$CMeO\cdot C(N_2HPh)\cdot CH_2\cdot CHMe_2,$$

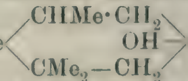
which crystallises in yellow needles melting at 94°, and gives an *osazone* melting at 115—116°.

The oily product obtained by treating isonitrosoethyl isobutyl ketone with nitric peroxide contains, in addition to dinitroethane and acetylisovaleryl, *isovaleryldinitroethane*, $CMe(NO_2)_2\cdot CO\cdot CH_2\cdot CHMe_2$, which crystallises in broad laminæ melting at 65—66°, and may be also prepared by the action of nitric acid on ethyl isobutyl ketone.

On treating isonitrosomethyl ethyl ketone with nitric peroxide as described above, an oily *substance*, probably acetyldinitroethane, $CMeAc(NO_2)_2$, is obtained. W. J. P.



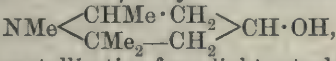
Tropeines of the Triacetonamine Series. By CARL D. HARRIES (*Annalen*, 1897, **296**, 328—343. Compare this vol., i, 293).—*av-Dimethylvinyldiacetonalkammonium iodide*, $NMe_2I\Big\langle\begin{array}{l}CHMe\cdot CH_2\\ \qquad OH\rightarrow\\ CMe_2-CH_2\end{array}\Big\rangle CH$, is obtained by the action of methylic iodide on α-vinyldiacetonalkamine (this vol., i, 295), dissolved in methylic alcohol, at the ordinary temperature; it crystallises from alcohol in plates, and decomposes about 270°. A portion of the original substance resists the action of methylic iodide, and after removing the foregoing salt, may be precipitated from the ethereal solution by means of light petroleum, in which it is but sparingly soluble; on evaporating the filtrate with hydrobromic acid, the *hydrobromide* of *av*-methylvinyldiacetonalkamine is obtained, and crystallises from absolute alcohol in six-sided plates. The *hydrate*, produced on treating the aqueous solution of the hydrobromide with caustic soda, melts at 39—40°, being precipitated in lustrous scales on adding light petroleum to the solution in benzene.



av-Methylvinyldiacetonalkamine, $NMe\Big\langle\begin{array}{l}CHMe\cdot CH_2\\ \qquad OH\rightarrow\\ CMe_2-CH_2\end{array}\Big\rangle CH$, is obtained as an oil on exposing the hydrate in the desiccator, and boils at 225—226° under a pressure of 744 mm.; the *aurochloride* crystallises from dilute hydrochloric acid in large plates, and the *platinochloride* forms microscopic prisms.

Application of the mandelic acid reaction to the substituted vinyldiacetonalkamines has led to results comparable with the observations of Liebermann and Limpach in connection with ψ-tropine (Abstr., 1892, 891); homatropine, and the corresponding mandelic derivative of the labile (β-)vinyldiacetonalkamine are definitely crystalline, whilst ψ-homatropine and the mandelic derivative of *av*-methylvinyldiacetonalkamine are oils.

a-Phenylglycolyl-v-methylvinyldiacetonalkamine,
$C_9H_{18}NO\cdot CO\cdot CHPh\cdot OH$,
is obtained by heating the methylated base dissolved in hydrochloric acid with mandelic acid on the water bath; it is an oil which does not dissolve readily in water, and has a strongly alkaline action on turmeric. When the alkaloid is evaporated in a porcelain dish with a few drops of fuming nitric acid, and the deep brown residue treated with alcoholic potash, a persistent orange coloration is developed. The *aurochloride* forms microscopic needles, but the salts generally are not characteristic. The alkaloid is very feebly anæsthetic, and does not induce mydriasis.

βν-Dimethylvinyldiacetonalkammonium iodide is obtained by the action of methylic iodide on β-vinyldiacetonalkamine. *βν-Methylvinyldiacetonalkamine*,  $NMe\!<\!\begin{matrix}CHMe\cdot CH_2\\ CMe_2-CH_2\end{matrix}\!>\!CH\cdot OH$, is produced along with it, and after crystallisation from light petroleum melts at 70—72°, and boils at 220° under a pressure of 744 mm.; treatment with a boiling solution of sodium amyloxide in amylic alcohol for 20 hours converts it into the stable modification. The *hydrochloride* is crystalline, the *aurochloride* forms prisms, and the *platinochloride* also crystallises.

β-Phenylglycolyl-v-methylvinyldiacetonalkamine crystallises from light petroleum in small, six-sided prisms melting at 113°; evaporation with fuming nitric acid, followed by treatment with alcoholic potash, develops a reddish-yellow coloration. The *hydrochloride* is a very hygroscopic micro-crystalline powder, and the *picrate* forms nodules; the *aurochloride* crystallises in golden-yellow plates, sinters at 150°, and melts at 158—159°, whilst the *platinochloride* forms oblique tabular crystals. The alkaloid induces mydriasis in rabbits and men, the maximum effect in the human subject being observed after the lapse of 40 minutes.

M. O. F.

Electrolysis of Trichloracetic Acid. By KARL ELBS and K. KRATZ (*J. pr. Chem.*, **55**, 502—505).—Trichloromethylic trichloracetate is formed on electrolysing either sodium trichloracetate or the zinc salt, and consists of white crystals melting at 34°; it is slowly decomposed by water, with formation of chloral and phosgene.

J. F. T.

Behaviour of Thioacetic Acid towards Salt Solutions. By N. TARUGI (*Gazzetta*, 1897, **27**, i, 316—328).—The black precipitate obtained with thioacetic acid and acid solutions of bismuth salts is always bismuth trisulphide, Bi_2S_3. *Bismuth thioacetate*, $Bi(COSMe)_3$, is deposited in long, transparent prisms, melting at 85°, on allowing a solution of bismuth hydroxide in excess of thioacetic acid to evaporate spontaneously. When warmed, in presence of air, with a small quantity of water, the new salt decomposes in accordance with the equation $2Bi(COSMe)_3 + H_2O + O = BiS(COSMe)_3 + BiO(COOMe) + 2HCOSMe$; the *compound* of the composition $BiS(COSMe)_3$ is a red, amorphous powder insoluble in carbon bisulphide. On adding much water to bismuth thioacetate and then boiling, the following reaction occurs: $Bi(COSMe)_3 + 2H_2O = BiS(COSMe) + 2MeCOOH + H_2S$, and the *compound* of the composition $BiS(COSMe)$ separates as a dark-red powder. Ammonia, soda, sodium carbonate, hydrochloric acid and the alkaline sulphides convert bismuth thioacetate into the trisulphide. Cold concentrated sulphuric acid acts on the thioacetate in accordance with the equation $3Bi(COSMe)_3 + 4H_2SO_4 = Bi_2(SO_4)_3 + (COSMe)BiSO_4 + 8HCOSMe$, and the double *salt* of the composition $(COSMe)BiSO_4$ is deposited as a red powder; hot sulphuric acid converts the thioacetate into bismuth trisulphide. When dry bismuth thioacetate is heated, it first melts, and then decomposes in accordance with the equation $2Bi(COSMe)_3 = Bi_2S_3 + 3SAc_2$, thioacetic anhydride distilling.

On treating the compound of the composition $(COSMe)_3BiS$, with concentrated sulphuric acid, reaction occurs with evolution of heat, in accordance with the following equation: $(COSMe)_3BiS + H_2SO_4 = H_2S + (COSMe)_3BiSO_4$; the new *compound*, $(COSMe)_3BiSO_4$, is brown, and must be prepared in an atmosphere of some inert gas, such as carbonic anhydride. The compound of the composition $(COSMe)BiS$ reacts with concentrated sulphuric acid in accordance with the equation $(COSMe)BiS + H_2SO_4 = H_2S + (COSMe)BiSO_4$.

Bismuth tri-iodide, BiI_3, reacts with thioacetic acid in the cold, with formation of Muir and Eagles' bismuth sulphiodide (Trans., 1895, 90), in accordance with the following equation, $BiI_3 + H\cdot COSMe + H_2O = BiSI + MeCOOH + 2HI$. Iodine in carbon bisulphide solution converts bismuth thioacetate into a red, amorphous *substance* of the composition $(COSMe)BiI_2$. On treating bismuth potassium iodide with iodine and thioacetic acid in carbon bisulphide solution, a yellow, amorphous *substance* of the composition $(COSMe)_2BiI$ is obtained.

Some of the salts described above afford the first examples of quinquivalent bismuth amongst aliphatic compounds. W. J. P.

Isolauronolic Acid. By G. Blanc (*Compt. rend.*, 1897, **124**, 624—626. Compare this vol., i, 538).—When isolauronolic chloride (2 mols.) is treated with zinc-methyl (1 mol.) in the presence of anhydrous ether, the *ketone*, $C_{10}H_{16}O$, is formed. It is a colourless, mobile liquid having a powerful camphor-like odour, is insoluble in water, but soluble in all the ordinary organic solvents. It boils at 200—202°, has a sp. gr. = 0·9404 at 14°, and an index of refraction = 1·474 at 15°. It distils readily with steam. The *oxime*, $C_{10}H_{16}{:}NOH$, forms large, transparent, colourless, rhombic crystals melting at 64—65° and boiling at 140° (13 mm.). It is odourless. The *semicarbazone*, $C_{10}H_{16}{:}N\cdot NH\cdot CO\cdot NH_2$, occurs either as slightly yellow, leaf-like crystals or as fine needles melting at 49°. It is very soluble in ether and light petroleum, less soluble in alcohol. The *phenylhydrazone*, $C_{10}H_{16}{:}N\cdot NHPh$, is a viscous, yellow liquid boiling at 185—190° (13 mm.).

When the ketone is subjected to the action of nascent hydrogen in ethereal solution and the products of the reaction distilled under reduced pressure, two compounds are obtained, namely, an *alcohol*, $C_{10}H_{18}O$, and a substance having the formula $C_{20}H_{34}O_2$, probably a pinacone. The alcohol is a colourless, mobile liquid having a penetrating odour somewhat resembling that of the ketone; it boils at 205°, and is insoluble in water, but soluble in the ordinary organic solvents. The corresponding *chloride* and *acetate* can be obtained from it. The compound $C_{20}H_{34}O_2$ remains behind after distilling off the alcohol under reduced pressure;

when recrystallised from dilute alcohol, it melts at 120° and is but slightly soluble in alcohol, ether, or light petroleum. On distillation, it undergoes decomposition into the alcohol and the ketone.

A. C. C.

Composition of Some Oil Seeds. By ALEXANDRE HÉBERT (*Bull. Soc. Chim.*, 1896, [iii], 15, 935—941).—The author describes the examination of three seeds not previously studied, two of which come from the French Congo, whilst the third is obtained from a plant growing in San Salvador. The first seed described is known in the Congo by the name of *I'Sano* or *Unguecko*, and is obtained from a large tree belonging to the Olacineæ family. The decorticated seeds contain 37 per cent. of husk, the analysis of which is given, and 63 per cent. of kernel. The dried kernels yielded 60 per cent. of their weight of fat and oil. An analysis of the extracted residue shows that it contains 33·12 per cent. of proteids, and it would therefore be of value as a cattle food. The oil, which is of a reddish colour and has a sp. gr. = 0·973 at 23°, is viscous, very slightly soluble in 90 per cent. alcohol, and has strong drying properties. With monhydrated sulphuric acid, a rise of temperature of 117° is produced. On saponification and acidification with sulphuric acid, it yields 86 per cent. of brown liquid fatty acids, the lead salts of which are entirely soluble in ether. Fractional precipitation with baryta indicated the presence of three acids, the first being probably identical with oleic acid, the second with linoleic acid, whilst the third consists of a new unsaturated acid of the formula $C_{14}H_{20}O_2$, to which the name *isanic acid* is given (see Abstr., 1896, i, 638).

The second seed studied by the author is known as *Mohamba*, and in many respects resembles the preceding. It contains 35 per cent. of husk (of which an analysis is given) and 65 per cent. of kernel, yielding 12 per cent. of fat and oil. The oil is yellow and has a sp. gr. = 0·915 at 23°. With monhydrated sulphuric acid, it produces a rise of temperature of 55°, and yields 90 per cent. of liquid, insoluble fatty acids, the lead salts of which are completely soluble in ether. The mixed fatty acids, after standing for some time, deposit a white acid, soluble in alcohol and ether, from which it crystallises in plates melting at 34—35°. It unites with approximately the same amount of bromine as oleic acid, and appears to belong to the series $C_nH_{2n-2}O_2$, but does not correspond with any known acid. The liquid from which this solid separates consists of oleic acid.

The third seed is known as *Aceituno*, and is the product of the wild olive tree of Central America. The decorticated seeds yield 64 per cent. of husk and 34 per cent. of kernel. The latter, after extraction with light petroleum, yielded a residue containing a large proportion of tannin and of dextrose, but free from starch. The fat occurs as a yellow mass melting at 30°, which, on saponification and acidification with sulphuric acid, yields more than 90 per cent. of white, solid, fatty acids melting at 48—49°. Of these, about one-half consist of saturated and one-half of unsaturated acids, the former melting at 54—55°. By fractional precipitation with barium chloride, three barium salts were obtained from the mixed saturated acids, yielding acids melting at 58—59°, 44°, and 38° respectively.

A. C. C.

Some Malonic Acid Derivatives.—By Richard S. Curtiss (*Amer. Chem. J.*, 1897, 19, 691—701. Compare Bischoff, this vol., i, 267).—When ethylic bromomalonate, $CHBr(COOEt)_2$ (1 mol.), is allowed to remain at the ordinary temperature with aniline (3 mols.), *ethylic anilidomalonate*, $NHPh\cdot CH(COOEt)_2$, is formed; this crystallises in greenish-white, monoclinic prisms and melts at 44—45°. When heated with mercuric oxide and light petroleum at 95—100°, it is oxidised to *ethylic dianilidomalonate*, $(NHPh)_2C(COOEt)_2$, which is also formed when ethylic dibromomalonate (1 mol.) is left in contact with aniline (5 mols.); this substance melts at 117—118°, and distils with but little decomposition.

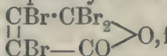
When ethylic dibromomalonate, mixed with a little alcohol, is dropped into alcoholic sodium ethoxide kept at 48—50°, ethylic diethoxymalonate is formed, together with some ethylic carbonate; if the temperature is kept at 10—15°, diethoxymalonate is formed in less amount, and none is obtained if 4 mols. of sodium ethoxide (instead of 2) are used per mol. of ethylic dibromomalonate; evidence was obtained in all cases of the formation of substances with the reactions of bromoform and of aldehyde, and a certain amount of the ethylic salts became hydrolysed, and some carbonic anhydride was usually evolved. If the sodium ethoxide is dropped into the ethylic dibromomalonate (at 30—40°), ethylic ethylenetetracarboxylate, $C_2(COOEt)_4$, is formed, together with a little ethylic carbonate, but no diethoxymalonate could be isolated from the product. C. F. B.

Derivatives of Bromomaleic and Chloromaleic Acid-aldehydes. By Henry Barker Hill and Eugene T. Allen (*Amer. Chem. J.*, 1897, 19, 650—667).—When pyromucic acid (1 mol.) is suspended in water and bromine (3 mols.) added gradually, the mixture being cooled and shaken, 2 mols. of bromine react readily, but the other one only slowly. The product is finally extracted with ether, and the residue from this extract treated with hydroxylamine hydrochloride, when *bromomaleic acid-aldoxime*, $NOH{:}CH\cdot C_2HBr\cdot COOH$, is formed, and may be purified from mucobromic acid and mucobromoxime by warming for a short time with a little water; the acid-aldehyde itself could not be isolated. This acid-aldoxime melts with explosive decomposition at about 143°; its *barium* salt, with $4H_2O$, and anhydrous *lead* and *silver* salts were prepared; its *methylic* salt, obtained by boiling a methyl-alcoholic solution of the acid after adding a very little strong sulphuric acid, melts at 152—153°. The acid-aldoxime itself is converted by heating with water at 110° into ammonium hydrogen bromomaleate; when it is dissolved in strong sulphuric acid and the solution poured gradually into carefully cooled water, it yields the *acid-aldoxime anhydride*, $C_4H_2BrNO_2$, which melts at 83° when pure; when this substance is heated above its melting point, it undergoes a molecular transformation into bromomaleimide, which cannot be obtained by heating the acid-aldoxime itself. When the acid-aldoxime is heated with acetic acid to which 20 per cent. of acetic anhydride has been added, and the mixture is then saturated with gaseous hydrogen chloride, chlorobromosuccinic acid, $C_4H_4BrClO_4$, is formed. If it is dissolved in methylic alcohol, and the solution saturated with gaseous hydrogen chloride or bromide, the methylic salts of *chlorobromo-* and *dibromo-succinic acid-aldoximes,* $C_4H_4BrCl(\text{or } Br_2)NO_3Me$, melting at 167—168° and 161—162°, are respectively formed. With dry bromine in chloroform solution at 75—80°, it forms *tribromosuccinic acid-aldoxime,* $C_4H_4Br_3NO_3$, melting at 133°; this loses hydrogen bromide and carbonic anhydride when it is warmed with water, forming *dibromacraldoxime,* $C_3H_3Br_2NO$, which melts at 104° or lower, and yields dibromacraldehyde when boiled with dilute hydrochloric acid, for the oily product, although it could not be obtained pure, is oxidised by silver oxide to $\alpha\beta$-dibromacrylic acid.

An analogous set of chlorine compounds was prepared by similar methods, starting with pyromucic acid (1 mol.), which was suspended in cooled hydrochloric acid, an amount of manganese dioxide just necessary to liberate 3 mols. of chlorine being then added gradually. *Chloromaleic acid-aldoxime* melts and decomposes at 150°; the *anhydride* melts at 58°, and the *methylic* salt at 130°. The *methylic* salts of *dichlorosuccinic* and *bromochlorosuccinic acid-aldoximes* melt at 135° and 145° respectively; the second must be isomeric with the chlorobromo-compound described above.

Incidentally, *mucochloroxime anhydride* was prepared from the oxime by treatment with sulphuric or hydrochloric acid; it melts at 76—77°.

C. F. B.

Absorption of Oxygen by Tetrabromofurfuran. By HENRY A. TORREY (*Amer. Chem. J.*, 1897, 19, 668—671. Compare Hill and Hartshorn, Abstr., 1885, 762).—When tetrabromofurfuran, $\begin{matrix}\mathrm{CBr{:}CBr}\\ \mathrm{CBr{:}CBr}\end{matrix}{>}\mathrm{O}$, is exposed to direct sunlight for 6—7 hours in a flask through which dry oxygen is passed slowly, it becomes oxidised to a yellow substance which solidifies completely after a time, and which is doubtless dibromomaleic bromide,  $\begin{matrix}\mathrm{CBr{\cdot}CBr_2}\\ \mathrm{CBr{-}CO}\end{matrix}{>}\mathrm{O}$, for it forms dibromomaleic and hydrobromic acids when it is boiled with water. The gain in weight is only 80—85 per cent. of the theoretical, but this is due to the formation of some dibromomaleic anhydride from the bromide first formed; in fact, if the reaction is prolonged beyond 6—7 hours, a loss of weight is manifested, and bromine is evolved.

C. F. B.

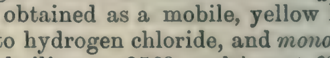
Exchange of Bromine for Chlorine in Aromatic Compounds. By RUDOLF WEGSCHEIDER (*Monatsh.*, 1897, 18, 329—346).—When concentrated hydrochloric acid acts on *s*-tribromaniline at a temperature of 200°, the latter is converted into *s*-trichloraniline. The conversion is, however, incomplete, on account of the hydrobromic acid formed during the process, which produces the opposite reaction, namely, exchange of chlorine for bromine. This explanation is supported by the fact that, when concentrated hydrobromic acid acts on *s*-trichloraniline, the tribromo-compound is formed, a second reaction taking place at the same time, namely, the substitution of bromine for hydrogen. As the reaction is carried out in sealed tubes, presumably the oxygen of the enclosed air acts on the hydrobromic acid, forming free bromine, which then replaces hydrogen. At a higher temperature, it should therefore be possible to replace more than three hydrogen atoms in aniline by bromine.

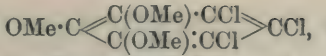
In hydrolysing *s*-tribromobenzonitrile containing chloro-*s*-tribromobenzene, concentrated hydrochloric acid was used. As *s*-tribromobenzoic acid was produced, it follows that there is no appreciable exchange of bromine for chlorine when either of these substances is acted on by hydrochloric acid.

Tribromaniline is acted on by cuprous chloride, reduction taking place, aniline and monobromo- and dibromo-derivatives of aniline being formed. Exchange of bromine for chlorine takes place only to a small extent.

The author discusses the theory of these and similar reactions at some length, and points out that Köhnlein's propositions (*Annalen*, **225**, 194) regarding the influence of the metal combined with a halogen on the exchange of a halogen element between an inorganic and an organic halogen compound do not hold good in general, but must be provisionally confined to the exchange of halogen with organic compounds possessing no basic character, and in which the halogen enters an open chain.
A. W. C.

Some Derivatives of Anethoil. By GEORGES DARZENS (*Compt. rend.*, 1897, **124**, 563—565).—*Anethoil dichloride* is prepared by slowly pouring a solution of chlorine (1 mol.) in carbon tetrachloride into a well cooled solution of anethoil (1 mol.) in three times its weight of the same solvent. After distilling off the carbon tetrachloride under reduced pressure, the dichloride is obtained as a mobile, yellow liquid which, on distillation, breaks up into hydrogen chloride, and *monochloranethoil*, $\mathrm{OMe{\cdot}C_6H_4{\cdot}C_3H_4Cl}$ [1 : 4], boiling at 258°, melting at 6°, and having a sp. gr. = 1·135 at 0°. It has an odour of the oil of anise, and is identical with the derivative obtained by Ladenburg by the action of phosphorus pentachloride on anethoil. *Monochloranethoil dichloride* is obtained by treating the preceding compound with a solution of chlorine in carbon tetrachloride. It is a white, crystalline substance melting at 35° and soluble in all the ordinary organic solvents. *Monochloranethoil dibromide*, prepared by treating monochloranethoil with a solution of bromine in carbon tetrachloride, is a white, crystalline substance melting at 45°. The odour of anethoil is not modified by the substitution of chlorine for hydrogen in the side-chain.
A. C. C.

Trichlorotrimethylphloroglucinol and Trichlorotrimethylpyrogallol. By PIETRO BARTOLOTTI (*Gazzetta*, 1897, **27**, i, 289—291).—*Trichlorotrimethylphloroglucinol*,  $\mathrm{OMe{\cdot}C}{<}\begin{matrix}\mathrm{CCl{\cdot}C(OMe)}\\ \mathrm{CCl{:}C(OMe)}\end{matrix}{>}\mathrm{CCl}$, is prepared by passing dry chlorine through a hot acetic acid solution of trimethylphloroglucinol, precipitating the solution with water, and distilling the deposit in a current of steam; it crystallises in thin, white needles melting at 130—131°, and is identical with the product obtained by Ciamician and Silber on treating methylhydrocotoin or methylprotocotoin with phosphorus pentachloride. A mixture of chlorinated products is obtained by chlorinating trimethylphloroglucinol in the cold.

Trichlorotrimethylpyrogallol,  $OMe\cdot C\begin{smallmatrix}\diagup C(OMe)\cdot CCl \diagdown \\ \diagdown C(OMe){:}CCl \diagup\end{smallmatrix}CCl$, obtained by the direct chlorination of trimethylpyrogallol in cold acetic acid solution, is purified by the method used above for its isomeride; it separates from alcohol in beautiful crystals melting at 54°.

W. J. P.

Halogen Addition-products of the Anilides. By Henry Lord Wheeler, Bayard Barnes, and Julius Howard Pratt (*Amer. Chem. J.*, 1897, **19**, 672—682. Compare Abstr., 1896, 1367.)—Ammonium tri-iodide, NH_4I,I_2, obtained by evaporating a solution of the calculated quantity of iodine in concentrated aqueous ammonium iodide, crystallises in rhombic prisms $[a:b:c = 0{\cdot}6950:1:1{\cdot}1415]$, and is isomorphous with the corresponding trihaloids of potassium, rubidium, and cæsium. The trihaloids of the anilides are quite dissimilar, crystallising in the monoclinic or triclinic system. The hydrogen-haloids were prepared by passing the dry halogen haloid into a solution of the anilide in ethylic acetate, chloroform, or benzene; by dissolving them in hot glacial acetic acid, adding the calculated quantity of iodine or bromine, and allowing the solution to cool, or to evaporate spontaneously, crystals of the perhaloids are obtained; these are more or less red in colour, and are darker the more iodine they contain. The following compounds were prepared:

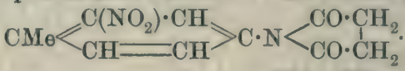
$NHAcPh,HCl,I_2$. $NHAcPh,HBr$. $NHAcPh,HBr,I_2$; triclinic $[a:b:c = 0{\cdot}5707:1:1{\cdot}2005; \alpha = 89°\ 26', \beta = 132°\ 20', \gamma = 83°\ 16']$. $(NHAcPh)_2,HI$. $(NHAcPh)_2,HI,I_2$; triclinic $[\alpha = 102°\ 56', \beta = 104°\ 34', \gamma = 113°\ 2']$. $(C_6H_4Br\cdot NHAc)_2,HCl$ [1 : 4]. $(C_6H_4Br\cdot NHAc)_2,HCl,I_2$. $(C_6H_4Br\cdot NHAc)_2,HBr,I_2$. $(C_6H_4Br\cdot NHAc)_2,HI$. $(C_6H_4Br\cdot NHAc)_2,HI,I_2$; triclinic (? *mono*-clinic) $[a:b:c = 1{\cdot}853:1:3{\cdot}015; \beta = 79°\ \tfrac{1}{2}']$. $(C_6H_4Br\cdot NHAc)_2,HI,I_4$. $NO_2\cdot C_6H_4\cdot NMeAc,HBr$ [1 : 3]. $(NO_2\cdot C_6H_4\cdot NMeAc)_2,HBr,Br_2$. $(NO_2\cdot C_6H_4\cdot NMeAc)_2,HBr,I_4$. $(NHPh\cdot CHO)_2,HCl$. $(NHPh\cdot CHO)_2,HI$. $NHPh\cdot CHO,HI$. $(NO_2\cdot C_6H_4\cdot NHAc)_2,HCl$ [1:3].

C. F. B.

Mercurioaniline. By Leone Pesci (*Gazzetta*, 1897, **27**, i, 567—574).—The author has previously obtained mercurioaniline (Abstr., 1892, 1448), and also paramercuriodiphenylenemercuriodiamine (Abstr., 1894, i, 248). Mercurioaniline reacts with sodium thiosulphate, potassium iodide, ammonium bromide, and carbon bisulphide in accordance with the equations $(NHPh)_2Hg + Na_2S_2O_3 + 2H_2O = HgS_2O_3 + 2NH_2Ph + 2NaOH$. $(NHPh)_2Hg + 2KI + 2H_2O = HgI_2 + 2NH_2Ph + 2KOH$. $(NHPh)_2Hg + 2NH_4Br = HgBr_2 + 2NH_2Ph + 2NH_3$. $(NHPh)_2Hg + CS_2 = HgS + (NHPh)_2CS$. On comparing these reactions with those of paramercuriodiphenylenemercuriodiamine (Piccinini, Abstr., 1895, i, 358), it will be seen that, in the latter case, the reagent acts, just as in the above reactions, on the mercury attached to nitrogen, whilst the mercury attached to the phenylene nucleus is not attacked and gives paramercurioaniline; the latter has the constitution $Hg(C_6H_4NH_2)_2$, and is an isomeride of mercurioaniline, $Hg(NHPh)_2$, containing mercury attached to nitrogen only. Mercurioaniline is converted by acids into aniline and a mercuric salt; by treatment with mercuric acetate, it gives the *diacetate* of paramercuriodiphenylenemercuriodiamine, $\mathrm{Hg}{<}\begin{matrix}C_6H_4\cdot NH(OAc)\\ C_6H_4\cdot NH(OAc)\end{matrix}{>}\mathrm{Hg}$, which crystallises in yellow, transparent needles soluble in acetic acid. W. J. P.

Preparation of 1 : 2 : 3-Metaxylidine. By Arturo Miolati and Alfredo Lotti (*Gazzetta*, 1897, **27**, i, 293—299).—Luhmann (*Annalen*, 1860, **113**, 274,) and Bussenius and Eisenstuck (*Annalen*, **114**, 156), by treating metaxylene with fuming nitric acid, obtained the following trinitroxylene, $\mathrm{CH}{<}\begin{matrix}C(NO_2)\cdot CMe\\ C(NO_2):CMe\end{matrix}{>}C\cdot NO_2$, which, when reduced with hydrogen sulphide in ammonia solution, gives a mixture of a monamine with the diamine, $\mathrm{CH}{<}\begin{matrix}C(NH_2)\cdot CMe\\ C(NH_2):CMe\end{matrix}{>}C\cdot NO_2$; the latter may be converted into 2-nitrometaxylene, either by passing nitrous fumes into its boiling alcoholic solution, or by adding cooled ethylic nitrite to a concentrated solution of its sulphate in dilute alcohol and then gradually raising the mixture to the boiling point. The nitroxylene, when reduced by iron and acetic acid, gives 1 : 2 : 3-metaxylidine boiling at 210—212°, as stated by Nölting and Forel (Abstr., 1886, 58).

Paratolilsuccinimide, when treated with fuming nitric acid, yields a *compound* which crystallises in yellow laminæ melting at 137°; its decomposition by potash shows it to have the constitution



$$\mathrm{CMe}{<}\begin{matrix}C(NO_2)\cdot CH\\ CH{=\!=}CH\end{matrix}{>}C\cdot N{<}\begin{matrix}CO\cdot CH_2\\ CO\cdot CH_2\end{matrix}.$$

The succinimide of the composition $\mathrm{CH}{<}\begin{matrix}CMe\cdot CH\\ CMe:CH\end{matrix}{>}C\cdot N{<}\begin{matrix}CO\cdot CH_2\\ CO\cdot CH_2\end{matrix}$, on nitration, gives two products, one of which, on hydrolysis, yields a previously unknown nitroxylidine. W. J. P.

Combination of Metallic Salts with the Homologues of Aniline and their Isomerides. By D. Tombeck (*Compt. rend.*, 1897, **124**, 1531—1534. Compare this vol., i, 463).—When alcoholic solutions of toluidine and of the halogen salts of zinc or cadmium are mixed, compounds of the type $M''X_2,2C_7H_7\cdot NH_2$ are formed. The zinc salts crystallise in small, white needles, and all the compounds alter rapidly and become discoloured when exposed to air; when gently heated, toluidine is liberated. Cupric chloride, bromide, and iodide form very unstable compounds analogous to the aniline compound $CuCl_2,2NH_2Ph$ described by Destrem.

Xylidine yields similar compounds with the chlorides, bromides, and iodides of zinc and cadmium, and their formation is accompanied by a distinct development of heat.

Picoline behaves similarly; the compounds are of the same type, and form colourless crystals. Lutidine and collidine likewise yield analogous compounds which crystallise well.

All these compounds are but slightly soluble in water; the organic base is slowly liberated at the ordinary temperature and more rapidly on heating. They have a distinct vapour pressure at the ordinary temperature, and when thrown on water show movements similar to those of camphor.

Bases derived from aniline by substitution behave in the same way as the homologues and their isomerides. C. H. B.

Nitrosodiphenylmethylamine. By CH. CLOËZ (*Compt. rend.*, 1897, **124**, 898—901).—The ease with which nitrosodimethylaniline can be prepared from dimethylaniline led the author to endeavour to prepare a dinitroso-derivative from diphenylmethylamine by the action of nitrous anhydride. This was, however, found to be impossible, the mononitroso-derivative alone being always formed. A solution of sodium nitrite (15 grams) in water (70 grams) was added drop by drop to a solution of diphenylmethylamine (40 grams) in hydrochloric acid solution of sp. gr. = 1·165 (200 grams) cooled to − 10°. After some time, crystals of the hydrochloride of nitrosodiphenylmethylamine separated, from which the base was prepared by dissolving in water and precipitating with sodium carbonate. It crystallises from methylic alcohol in fine green plates melting at 44°, and is very stable. With dimethylmetamidophenol, the hydrochloride of this base forms a fine blue-colouring matter, which is readily fixed on cotton mordanted with tannin. When two parts of nitrosodiphenylmethylamine are treated with three parts of gallic acid, a product is obtained which is soluble in sodium carbonate solution and which dyes wool and silk a violet-blue. It is also fixed by cotton treated with metallic mordants or with tannin.

Sulphonic Derivative of Diphenylmethylamine, $NMePh\cdot C_6H_4\cdot SO_3H$.—185 grams of the base is heated for 10 hours at 160° with 100 grams of ordinary sulphuric acid. At the end of this time, the mixture is treated with a solution of caustic soda, filtered, evaporated to dryness, and the dry residue extracted with boiling alcohol. On evaporation, a crystalline mass of the sodium salt of the above sulphonic acid is obtained; it is very soluble in alcohol and in water, from which it crystallises in small, granular masses consisting of microscopic needles. The acid itself is very soluble in alcohol and in water, but almost insoluble in solutions of hydrochloric acid, strong or dilute. It could not be obtained in a state of purity. On treating a mixture of the sodium salt and sodium nitrite in molecular proportion with hydrochloric acid, a nitroso-derivative is formed. With dimethylmetamidophenol, this nitroso-compound yields a blue colouring matter, and with gallic acid a bluish-violet colouring matter which readily dyes wool, the tint produced resembling certain of the indulines. A. C. C.

Combination of Phenylhydrazine with Metallic Bromides. By JOSEPH MOITESSIER (*Compt. rend.*, 1897, **124**, 1306—1308).—Compounds of phenylhydrazine with metallic bromides are obtained by mixing alcoholic or aqueous solutions of the two substances. Zinc bromide yields $ZnBr_2,2N_2H_3Ph$, which forms anhydrous, white, rectangular lamellæ. Cadmium bromide forms an analogous compound which crystallises in long, quadrangular lamellæ, likewise anhydrous. The magnesium compound is analogous in composition, and crystallises in a similar form. Nickel and cobalt bromides behave similarly, and the iodides of the metals of the magnesium group likewise combine with phenylhydrazine.

Solutions of the compounds give the reactions of the metallic bromides and phenylhydrazine. C. H. B.

Combination of Phenylhydrazine with Metallic Iodides. By JOSEPH MOITESSIER (*Compt. rend.*, 1897, **124**, 1529—1531).—The compounds described are obtained by adding phenylhydrazine to an alcoholic solution of the particular iodide. Zinc iodide yields the compound $ZnI_2,2NHPh\cdot NH_2$, which crystallises in prisms and elongated rhomboidal lamellæ, and melts at about 175°. In presence of excess of phenylhydrazine, a second compound, $ZnI_2,5NHPh\cdot NH_2$, is formed, and crystallises in white prisms and quadrangular lamellæ; this melts at about 70°, decomposes at about 90°, and is soluble in water and organic solvents. The cadmium compound, $CdI_2,2NHPh\cdot NH_2$, forms minute needles, and the manganous compound is similar in composition and crystalline form; both decompose before melting. The cadmium compound is only slightly soluble in water and cold alcohol, and is insoluble in chloroform; the manganese compound is very soluble in water or alcohol, but quite insoluble in ether or chloroform. The nickel compound, $NiI_2,6NHPh\cdot NH_2$, forms microscopic lamellæ which decompose below 100° and are soluble in water or alcohol, especially when heated, but are only slightly soluble in ether and chloroform.

All these compounds lose phenylhydrazine when heated; if heated strongly in presence of air, they lose iodine also, and a residue of metallic oxide is left. Their solutions give the reactions of phenylhydrazine and the particular iodide. (Compare preceding abstract). Nitrates of the metals of the magnesium series form similar compounds. C. H. B.

Final Contribution to the Question of the Diazo-isomerism. By CHRISTIAN WILHELM BLOMSTRAND (*J. pr. Chem.*, **55**, 481—501).—Polemical matter relating to the Hantzsch-Bamberger controversy.

Action of Paradiazotoluene Nitrate and Sulphate on Methylic Alcohol. By WILLIAM E. CHAMBERLAIN (*Amer. Chem. J.*, 1897, **19**, 531—547. Compare Remsen and Dashiell, Abstr., 1893, i, 325).—The action of methylic alcohol on a paradiazotoluene salt, $C_6H_4Me\cdot N_2X$, may, of course, yield either paramethoxytoluene, $C_6H_4Me\cdot OMe$, or toluene, C_6H_5Me (the alcohol acting as a reducing agent), or both; nitrophenols are also obtained when the diazo-nitrate is used. The yield of the methoxy-compound is greater when the sulphate is used, and greater also when the reaction is carried out under diminished pressure. The following table shows the variety of conditions under which the reaction was effected, and gives the yields of the products in percentages of the theoretical :—

	Nitrate.		Sulphate.	
	Methoxy-toluene.	Toluene.	Methoxy-toluene.	Toluene.
With alcohol, ordinary pressure..........	29	trace	66	trace
,, diminished ,, ...	22	10	77	trace
,, increased ,, ...	39	—	61	trace
With NaOMe	—	36	—	32
With alcohol and KOH	—	44	—	59
,, K_2CO_3	—	53	—	44
,, zinc dust.................	—	*	—	46
,, zinc oxide	17	22	20	48

* No record ; about the same as the sulphate.

The diminution or increment of the pressure was 500 mm., as compared with the atmospheric pressure. The weight of alcohol used varied from about 2½ to 4 times the weight of the diazo-salt, whilst the weights of sodium (to make NaOMe), KOH, and K_2CO_3 added varied from 6—7, 10—12, and 27—13 per cent. of the alcohol respectively. Heat was used to promote the reaction when necessary; it is interesting to notice that potassium hydroxide, in solution in methylic alcohol, only acts very slowly on the diazo-salt at the ordinary temperature. No diphenyl was obtained in any case (Beeson, Abstr., 1894, i, 329).

The action of dilute nitric acid on paramethoxytoluene yields dinitrocresol melting at 80·5°. This makes it probable that, when nitrophenols are obtained by the reaction of diazo-nitrates with alcohol, these products result from the hydrolysis of alkoxy-compounds first formed, the introduction of nitro-groups taking place at the same time.

C. F. B.

Reaction of Nitrodiazobenzene and Diazobenzoic Acid Salts with Methylic Alcohol. By GEORGE F. WEIDA (*Amer. Chem. J.*, 1897, 19, 547—561. Compare Remsen and Graham, Abstr., 1889, 975).—The reaction was carried out by heating the diazo-salts on the water bath with 5 to 10 times their amount of methylic alcohol in a reflux apparatus, carefully regulating the temperature at first, and heating finally to 100°. With orthonitrodiazobenzene sulphate, the only product that could be detected was nitrobenzene, and the yield was 87 per cent. of the theoretical. Metanitrodiazobenzene nitrate yields nitrobenzene (51 per cent.) and a little metanitranisoil (metanitromethoxybenzene). Paranitrodiazobenzene nitrate yields both nitrobenzene (47—40 per cent.) and paranitranisoil (8—17 per cent.).

Ortho-, meta-, and para-diazobenzoic acid sulphates, and also the ortho- and para-nitrates, when heated with methylic alcohol, yield the corresponding methylic methoxybenzoates as the chief products. The ortho-nitrate yields also some asymmetrical nitrosalicylic acid [1 : 2 : 4], and the ortho-sulphate yields some methylic benzoate. It is remarkable that the meta-salt yields no benzoate, for it is known to yield ethylic benzoate when heated with ethylic alcohol. In the case of the para-nitrate, some free methoxybenzoic acid was obtained.

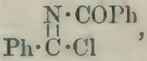
C. F. B.

Action of Methylic Alcohol on Orthodiazotoluene Sulphate. By WILLIAM BROMWELL (*Amer. Chem. J.*, 1897, **19**, 561—577. Compare Remsen and Orndorff, Abstr., 1888, 268).—Orthodiazotoluene sulphate is decomposed by methylic alcohol, both at the ordinary temperature and on the water bath; the product is almost entirely orthomethoxytoluene, $OMe\cdot C_6H_4\cdot CH_3$, only a trace of toluene being formed. Orthomethoxytoluene is oxidised by permanganate to orthomethoxybenzoic acid, $OMe\cdot C_6H_4\cdot COOH$, and when sulphonated with concentrated sulphuric acid at the ordinary temperature, it yields but one derivative, a *mono*sulphonic acid, $OMe\cdot C_6H_3(SO_3H)\cdot CH_3$; this melts at 212°; the *sodium* salt, with $5\frac{1}{2}H_2O$; *potassium* (from alcohol with $\frac{1}{2}H_2O$); *calcium*, with $9H_2O$; *barium* (from dilute solutions in shining transparent plates with $2H_2O$, from concentrated solutions in white irregular opaque crystals with H_2O); *magnesium*, with $5\frac{1}{2}H_2O$; *zinc*, with $6\frac{1}{2}H_2O$; *lead*, with $6H_2O$; and *copper*, with $6H_2O$, salts were prepared, and so were the *sulphonic chloride* and *sulphonamide*. The sulphonamide melts at 137°, and is oxidised by permanganate to *orthomethoxysulphaminebenzoic acid*, $OMe\cdot C_6H_3(SO_2\cdot NH_2)\cdot COOH$, which melts at 211°; no satisfactory result was obtained when this acid was fused with potassium hydroxide (compare Walker, this vol., i, 569).

Other interesting observations are that the nitrate of orthodiazotoluene is dangerously explosive, and that the substance sold in the State of New York as "Columbian spirit" is methylic alcohol, containing a little water, but otherwise quite pure. C. F. B.

Rearrangement of Oximido-derivatives. By ERNST OTTO BECKMANN [and K. SANDEL] (*Annalen*, 1897, **296**, 279—294. Compare Abstr., 1893, i, 474).—The existence of an unstable intermediate compound arising from the action of phosphoric chloride on α-benzilmonoxime has been already indicated (*loc. cit.*); this substance, which behaves in accordance with the constitutional formula, CPhCl:N·COPh, has now been isolated.

Benzoylbenzimide chloride,



$\begin{matrix}N\cdot COPh\\ \|\\ Ph\cdot C\cdot Cl\end{matrix}$

, is obtained by dissolving α-benzilmonoxime in anhydrous ether and treating the carefully cooled solution with phosphorus pentachloride; if the liquid is not cooled with ice, dibenzamide, ammonia, and benzoic acid are the products. This chloride, which crystallises from light petroleum and melts at 84°, gradually undergoes spontaneous change, yielding benzoic chloride and dibenzamide. When treated with dilute hydrochloric acid at 70—80°, it is scarcely changed at first, but if the liquid is boiled in a reflux apparatus, complete hydrolysis takes place; water produces the same effect, but the substance crystallises from absolute alcohol. The *benzoyl* derivative of γ-benzilmonoxime is obtained as a bye-product when benzoylbenzimide chloride is crystallised from absolute alcohol; it melts at 137°, and yields γ-benzilmonoxime when treated with alcoholic potash. Alkalis, alkali carbonates, carbamide, and moist silver oxide give rise to benzonitrile, whilst hydroxylamine converts the chloride into dibenzenylazoxime. When ammonia is passed into the benzene solution, benzoylbenzamidine, $NH{:}CPh{\cdot}NH{\cdot}COPh$, is produced; this substance is identical with the amidine obtained by Pinner from benzonitrile and sulphuric acid.

Benzoylphenylbenzamidine, $NPh{:}CPh{\cdot}NH{\cdot}COPh$, is obtained by adding aniline to a solution of the chloride in absolute alcohol, and after crystallisation from ether melts at 143°; cold hydrochloric acid resolves the substance into dibenzamide and aniline, and hot water produces the same effect, but the compound resists the action of alkalis. Hydroxylamine liberates aniline, and gives rise to dibenzenylazoxime.

Benzoylbenzylbenzamidine, $CH_2Ph{\cdot}N{:}CPh{\cdot}NH{\cdot}COPh$, produced by the action of benzylamine on the chloride dissolved in ether, melts at 147°. Secondary bases do not yield amidines, but give rise to benzo nitrile and benzoic acid.

Hydrazinebenzoylbenzamidine, $NH_2{\cdot}N{:}CPh{\cdot}NH{\cdot}COPh$, is prepared from benzoylbenzamide chloride and hydrazine, and after crystallisation from alcohol, melts at 189°. Compared with the foregoing amidine, it is a remarkably stable substance. Hot concentrated hydrochloric acid dissolves it slowly, but without effecting hydrolysis, and it is equally indifferent towards concentrated alkalis; it also resists the action of oxidising and reducing agents. The *hydrochloride* melts at 220—223°; the *phenylsulphone* derivative is obtained by agitation with benzenesulphonic chloride.

Phenylhydrazinebenzoylbenzamidine, $NHPh{\cdot}N{:}CPh{\cdot}NH{\cdot}COPh$, obtained when the chloride is gently heated with alcohol and phenylhydrazine, melts at 105°; it forms a *hydrochloride* and a *phenylsulphone* derivative.

Benzoylphenylmethylbenzamidine, $NMePh{\cdot}N{:}CPh{\cdot}NH{\cdot}COPh$, is produced by the action of phenylmethylhydrazine on the chloride, and melts at 125°. It is less stable than the hydrazine and phenylhydrazine derivatives, yielding ammonia, benzoic acid, and methylaniline when treated with boiling dilute hydrochloric acid; it resists the action of alkalis.

The foregoing amidines are also produced when benzoylbenzamidine is heated with the corresponding base. M. O. F.

The Difference between Ethers and Salts, considered in relation to the Constitution of the Rosanilines. By AUGUSTE ROSENSTIEHL (*Bull. Soc. Chim.*, 1895, [iii], 15, 952—959).—The author dissents from the view expressed by Tortelli (Abstr., 1895, i, 540) that, because the rosanilines react readily with certain reagents in aqueous solution, they are to be regarded as salts rather than ethers, silver nitrate, for instance, bringing about the precipitation of the whole of the chlorine in the hydrochloride, whilst the addition of barium chloride to a solution of the sulphate causes the precipitation of the theoretical quantity of barium sulphate. It is pointed out that no sharp distinction, based upon the ease with which their electro-negative elements or radicles are removed by certain reagents, can be drawn between *salts* on the one hand, and *ethers* on the other. Triphenylchloromethane, for example, reacts readily with silver nitrate, whilst the acetochlorides of iron prepared by Scheurer-Kestner, are but slowly acted on by the same reagent. Again, a freshly prepared solution of the double sulphate, obtained by heating chrome alum at 110°, gives no precipitate with barium chloride. In the case of the ethers, the double decomposition resulting in the removal of their electronegative elements or radicles is preceded by the hydrolysis of the ethers, and the author considers it possible that, in the case of slowly reacting salts, such as those above instanced, a similar hydrating action is a necessary preliminary. A. C. C.

Hydrocyanorosaniline. By AUGUSTE ROSENSTIEHL (*Bull. Soc. Chim.*, 1896, [iii], **15**, 959—964).—The author combats the views expressed by Tortelli on the constitution of rosanilines, views based chiefly on the properties of Hugo Müller's rosaniline hydrocyanide and that which Tortelli obtained from the double cyanide of pararosaniline and mercury (Abstr., 1895, i, 540). He gives reasons for maintaining that his pararosaniline formula is more in accordance with known reactions than those proposed by Fischer and by Nietzki.

A. C. C.

Derivatives of Benzophenone. By PIETRO BARTOLOTTI (*Gazzetta*, 1897, **27**, i, 280—288).—The author describes a more rapid process than the one he has previously given (this vol., i, 193) for preparing benzoguaiacol directly from guaiacol.

Acetylbenzoguaiacol, $COPh\cdot C_6H_3(OMe)\cdot OAc$, is prepared by heating benzoguaiacol with acetic anhydride and dry sodium acetate on an oil bath; it crystallises in colourless prisms melting at 105—106°, and is insoluble in soda.

Benzoylveratrol (methylbenzoguaiacol), $COPh\cdot C_6H_3(OMe)_2$ [$(OMe)_2 =$ 1:2], may be prepared by heating benzoguaiacol with methylic iodide and potash, or by heating veratrol with benzoic chloride and zinc chloride; it separates from alcohol in white crystals which melt at 101—102°.

Dinitrobenzoguaiacol, $COPh\cdot C_6H(NO_2)_2(OMe)\cdot OH$, is prepared by gradually adding an acetic acid solution of benzoguaiacol to fuming nitric acid; it separates from alcohol in thin, yellow crystals melting at 188—189°, and dissolves in hot soda, but separates as an oil on cooling.

1:2-*Dihydroxybenzophenone*, $COPh\cdot C_6H_3(OH)_2$, separates from the hydriodic acid mother liquors obtained during the determination of methoxyl in benzoguaiacol, acetylbenzoguaiacol and benzoylveratrol by Zeisel's method; it crystallises from water in long, white prisms containing $1H_2O$, which is lost at 110°; it then melts at 134°. It is probably identical with Döbner's benzoylpyrocatechol (Abstr., 1882, 507), although the latter is said to melt at 145°; both give a dibenzoyl-derivative melting at 95°, and a green colour with ferric chloride, changing to red on the addition of ammonium carbonate. W. J. P.

Parabenzoyltoluene Derivatives. By PAUL BOURCET (*Bull. Soc. Chim.*, 1896, [iii], **15**, 945—952).—For the preparation of the necessary parabenzoyltoluene, the author finds the method of Friedel and Crafts by far the most satisfactory. By employing a large excess of toluene (1000 grams of toluene, 50 grams of aluminium chloride, and 100 grams of benzoic chloride), and by adding the benzoic chloride little by little to the mixture of toluene and aluminium chloride, the formation of greenish, viscous bye-products, which are very difficult to remove, is avoided, and 92 per cent. of the theoretical yield can be obtained.

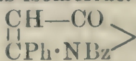
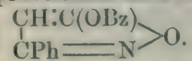
Parabenzoylbenzylic bromide, $C_6H_4Bz\cdot CH_2Br$, is obtained by heating a mixture of parabenzoyltoluene with bromine in molecular proportion at 150°. The viscous mass is thoroughly washed with cold water and dissolved in alcohol, ether, chloroform, light petroleum, or toluene, from any of which solvents it separates in colourless, monoclinic crystals, which are weakly birefractive, and melt at 96·6°. On oxidation with an alkaline solution of potassium permanganate, parabenzoylbenzoic acid, melting at 194—195°, is obtained. *Parabenzoylbenzylic alcohol*, $C_6H_4Bz\cdot CH_2\cdot OH$, is obtained by boiling 25 grams of the above bromide for 6 hours with 2 litres of a 2 per cent. solution of potassium carbonate. After several crystallisations from boiling water, it forms nacreous, feathery plates (monoclinic) melting at 48·3°. It is very slightly soluble in cold, but fairly soluble in hot water, and is very soluble in alcohol, ether, chloroform, and acetone. The *acetate*, $C_6H_4Bz\cdot CH_2\cdot OAc$, is prepared by boiling parabenzoylbenzylic bromide with a large excess of a 3 per cent. solution of potassium acetate for 6 hours. After filtering off the unattacked bromide, the filtrate is evaporated to dryness and extracted with ether, from which the acetate separates in slender needles melting at 36°. It is very soluble in hot water, slightly less in cold, and very soluble in alcohol, ether, acetone, and chloroform.

Parabenzoyldiphenylmethane, $C_6H_4Bz\cdot CH_2\cdot C_6H_5$, prepared by acting on parabenzoylbenzylic bromide (25 grams) with benzene (250 grams) in the presence of aluminium chloride (15 grams), is a colourless substance, crystallising in the rhombic system, and melting at 157°. It is very soluble in benzene, chloroform, or boiling acetic acid, only slightly so in cold water, alcohol, ether, and acetone, and almost insoluble in light petroleum.

Parabenzoylbenzylidenic dibromide, $C_6H_4Bz\cdot CHBr_2$, is prepared by allowing bromine (35 grams) to fall drop by drop into parabenzoyltoluene (24 grams) heated to 170°; the solid product crystallises from boiling alcohol in small, colourless, monoclinic crystals melting at 86·8° and soluble in ether, chloroform, and benzene. On oxidation with an alkaline solution of potassium permanganate, it yields parabenzoylbenzoic acid. *Parabenzoylbenzaldehyde*, $C_6H_4Bz\cdot COH$, is obtained from the preceding compound by heating it with water in sealed tubes for 10 hours at 180°, calcium carbonate being used to neutralise the hydrobromic acid formed. The liquid in the tubes, after filtration from the excess of calcium carbonate and from the unattacked bromide, deposits crystals as it cools, which, on recrystallisation from boiling water, separate in nacreous plates melting at 64·2°. It forms a crystalline compound with sodium hydrogen sulphite, and is very soluble in water, alcohol, ether, or chloroform, but insoluble in light petroleum, benzene, and toluene.

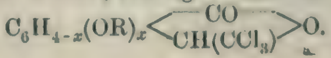
Parabenzoyltriphenylmethane, $C_6H_4Bz\cdot CHPh_2$.—Aluminium chloride (30 grams) is added gradually to a boiling solution of parabenzoylbenzylidenic dibromide (50 grams) in benzene (500 grams). After evaporating the excess of benzene, small, reddish crystals are obtained which are purified by repeated crystallisation from benzene or from boiling acetic acid. This substance forms small, rhombic crystals which are at first colourless, but become slightly red on exposure to the air; it melts at 164°. It is soluble in hot acetic acid, chloroform, or benzene, and slightly so in ether, alcohol, and light petroleum. *Parabenzoyltriphenylcarbinol*, $C_6H_4Bz{\cdot}CPh_2{\cdot}OH$, is obtained by oxidising the preceding compound, dissolved in glacial acetic acid, with an acetic acid solution of chromic acid, the latter being added little by little until the red colour remains permanent. On diluting with water, a white substance separates which can be purified by first dissolving it in glacial acetic acid, precipitating with water, and then crystallising it from boiling acetic acid. It forms large, colourless, monoclinic crystals melting at 158°, and is very soluble in chloroform, benzene, and glacial acetic acid, but only slightly so in alcohol, ether, or light petroleum.

A. C. C.

Isoxazolones [Phenylisoxazolones]. By Paul Rabe (*Ber.*, 1897, 30, 1614—1617. Compare Schiff, this vol., i, 444, 493, and Claisen, *ibid.*, 493).—Phenylisoxazolone, melting at 152°, reacts with benzoic chloride and sodium hydroxide solution, or, in benzene solution, with benzoic chloride and pyridine, yielding a mixture of two isomeric *benzoyl* derivatives. The α-derivative is formed in largest quantity by the Schotten-Baumann method, and it can be separated from the isomeric β-compound by recrystallisation from absolute alcohol, in which it is less soluble; it crystallises in colourless needles melting at 161°, and is readily soluble in ether and benzene, but insoluble in water, alkalis, or acids. Alcoholic potash readily hydrolyses it, as does also an acetic acid solution of phenylhydrazine, the latter yielding symmetrical benzoylphenylhydrazine and phenylisoxazolone. The *β-compound* is formed almost exclusively by the second method given above; it crystallises in colourless prismatic needles melting at 115°, and is insoluble in water, but dissolves in the usual organic solvents more readily than the α-compound. In chemical properties, it resembles its isomeride. The provisional formulæ given for the two compounds are  $\left.\begin{array}{l}\text{CH—CO}\\ \text{CPh}{\cdot}\text{NBz}\end{array}\right>\text{O}$ and  $\left.\begin{array}{l}\text{CH:C(OBz)}\\ \text{CPh}{=\!=}\text{N}\end{array}\right>\text{O}$.

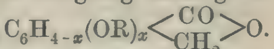
J. J. S.

Condensation Products of Chloral with Alkyl Derivatives of Metahydroxybenzoates and Symmetrical Dihydroxybenzoates: Synthesis of Alkylated Monhydroxy- and Dihydroxy-phthalic Acids. By Paul Fritsch (*Annalen*, 1897, 296, 344—361).—*Ethylic metamethoxybenzoate* boils at 163° under a pressure of 50 mm., and the *ethoxy*-derivative boils at 172—173° under a pressure of 50 mm.; *ethylic* 1 : 3 : 5-*dimethoxybenzoate* and *ethylic* 1 : 3 : 5-*diethoxybenzoate* melt at 26—27° and 19—20° respectively, and boil at 199—200° and 212° under a pressure of 50 mm.

When these salts are agitated with chloral hydrate and concentrated sulphuric acid, the corresponding substitution products of trichloromethylphthalide are formed, having a constitution represented by the general formula,  $C_6H_{4-x}(OR)_x\left<\begin{array}{c}\text{CO}\\ \text{CH(CCl}_3\text{)}\end{array}\right>\text{O}$. 5-*Methoxytrichloro-*

methylphthalide and 5-*ethoxytrichloromethylphthalide* melt at 135° and 118° respectively; 3 : 5-*dimethoxytrichloromethylphthalide* and 3 : 5-*diethoxytrichloromethylphthalide* melt at 125° and 113° respectively.

Treatment of the substituted trichloromethylphthalides with hot aqueous alkalis converts them into the phthalidecarboxylic acids, $C_6H_{4-x}(OR)_x<\begin{smallmatrix}CO\\CH(COOH)\end{smallmatrix}>O$. 5-*Methoxyphthalidecarboxylic acid* 5-*ethoxyphthalidecarboxylic acid*, 3 : 5-*dimethoxyphthalidecarboxylic acid*, and 3 : 5-*diethoxyphthalidecarboxylic acid* melt at 169—170°, 128°, 183°, and 172—173° respectively; the *methylic* salts melt at 95°, 79—80°, 142—143°, and 108° respectively.

Elimination of carbonic anhydride from the foregoing acids gives rise to the corresponding substituted phthalides,  $C_6H_{4-x}(OR)_x<\begin{smallmatrix}CO\\CH_2\end{smallmatrix}>O$. 5-*Methoxyphthalide*, 5-*ethoxyphthalide*, 3 : 5-*dimethoxyphthalide*, and 3 : 5-*diethoxyphthalide* melt at 120°, 87°, 166—167°, and 179° respectively.

Oxidation of the phthalides with potassium permanganate in alkaline solution converts them into the phthalic acids. 5-Methoxyphthalic acid and anhydride melt at 164° and 97°, and not, as stated by Schall, at 138—144° and 93° respectively. 3 : 5-*Dimethoxyphthalic acid* and 3 : 5-*diethoxyphthalic acid* melt at 158° and 182° respectively, and the *anhydrides* at 147° and 130°. Fusion of these acids with metadialkylamidophenols gives rise to rhodamines which dye animal fibre; sparingly soluble monosulphonic acids, which also behave as colouring matters, are obtained from these rhodamines by the action of fuming sulphuric acid.

If the oxidation of 5-methoxyphthalidecarboxylic acid is carried out with a solution of potassium permanganate at 60°, and the product neutralised with barium carbonate, the *barium* salt of 5-methoxyphthalonic acid, $COOH\cdot C_6H_3(OMe)\cdot CO\cdot COOH$, is obtained in transparent needles containing $2H_2O$. The phenylhydrazine *compound*, $C_{16}H_{12}N_2O_4$, crystallises in small needles, and melts at 223°; the metadimethylamidophenol *compound*, $C_{18}H_{17}NO_6$, becomes violet on exposure to the atmosphere, and melts at 180°. M. O. F.

Action of Potassium Hydroxide on Orthomethoxysulphaminebenzoic Acid. By CHARLES WALKER (*Amer. Chem. J.*, 1897, **19**, 578—580).—When *orthomethoxysulphaminebenzoic acid*

$$OMe\cdot C_6H_3(SO_2\cdot NH_2)\cdot COOH$$

(compare Bromwell, this vol., i, 564) is fused with potassium hydroxide at a dull red heat for 5 to 8 minutes, the product is *orthohydroxysulphaminebenzoic acid*, $OH\cdot C_6H_3(SO_2\cdot NH_2)\cdot COOH$; the stability of the sulphonamide group is remarkable. The new acid melts and decomposes at 231°; the *sodium* salt, with $1\frac{1}{2}H_2O$; *calcium*, with $6H_2O$; *barium*, with $4H_2O$, and *silver* salts were prepared and analysed.

When orthomethoxysulphaminebenzoic acid is heated with strong hydrochloric acid at 150—160° for 3 hours in a sealed tube, the product is salicylic acid. C. F. B.

Metadihydroxy-β-phenylcoumarin. By GIUSEPPE BRUNI (*Gazzetta*, 1897, **27**, i, 574—576).—Ciamician and Silber have described metamethoxyhydroxy-β-phenylcoumarin and its acetyl derivative as being yellow (Abstr., 1894, i, 255), although dihydroxyphenylcoumarin and its diacetate are both white; the author finds that the difference in colour is due to slight impurity, and not to difference of constitution. The two former substances are both white. W. J. P.

Action of Tannin on some Alkaloids. By WILLIAM OECHSNER DE CONINCK (*Compt. rend.*, 1897, **124**, 506—508).—When dry tannin is added to pyridine, it dissolves slowly without producing any precipitate, and the liquid, when left over sulphuric acid, dries up to a viscous, plastic mass insoluble in water; when tannin is added to a concentrated aqueous solution of pyridine, it behaves in a similar manner. Similar results are obtained when dry tannin is added to piperidine or nicotine, either pure or in concentrated aqueous solution.

When, however, concentrated aqueous solutions of tannin and of pyridine containing these substances in molecular proportion are mixed, a white precipitate is formed, consisting of a compound of 1 mol. of pyridine with 1 mol. of tannin. With piperidine, a similar result is obtained, but the white precipitate rapidly darkens. Experiments are recorded showing the extent to which solutions of pyridine and piperidine must be diluted in order to prevent their precipitation by tannin.

A. C. C.

Action of Tannin and of other Aromatic Derivatives on some Alkaloids and Compound Ureas. By WILLIAM OECHSNER DE CONINCK (*Compt. rend.*, 1897, **124**, 562—563).—Neither dry tannin nor an alcoholic solution of tannin gives any precipitate when added to a solution of pyridine in an equal volume of absolute alcohol, but on the addition of water a precipitate at once forms. With an alcoholic solution of piperidine, an emerald-green coloration is produced on the addition of dry tannin, and an immediate white precipitate on the addition of an alcoholic solution of tannin. Neither dry tannin nor an ethereal solution of tannin gives any precipitate when added to an ethereal solution of pyridine; a white precipitate is, however, formed on the addition of water. With an ethereal solution of piperidine, a solution of tannin in ether gives a precipitate, but dry tannin does not. The following reactions serve to readily distinguish between pyridine and piperidine.

A freshly prepared solution of gallic acid produces neither precipitate nor coloration when added to an aqueous solution of pyridine; with piperidine, a pale rose coloration is at first produced, becoming darker in colour, and finally of a deep yellow. With pyridine, pyrogallol gives a pale yellow coloration appearing only after some time, but with piperidine an immediate yellow coloration, becoming in turn deep yellow, dark brown, and brownish-black. Catechol gives no reaction with pyridine, but with piperidine a violet coloration at first, becoming successively pink and yellow.

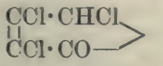
Quinol gives no reaction with pyridine, but with piperidine a yellow colour turning to a deep brown. Resorcinol, phloroglucinol, and orcinol give no reactions either with pyridine or piperidine in aqueous solution.

Tannin gives neither coloration nor precipitate when added to benzylcarbamide, diphenylcarbamide, phenylcarbamide, methylcarbamide, or diphenylthiourea in either aqueous, alcoholic, or ethereal solutions.

A. C. C.

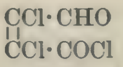
Preparation of Ethylic Phenylacetate. By WILHELM WISLICENUS (*Annalen*, 1897, **296**, 361—362).—Difficulty having sometimes arisen in preparing ethylic phenylacetate from benzylic cyanide, the author describes in detail the method which he adopts. M. O. F.

Oximes of Mucophenoxychloric and Mucophenoxybromic Acids; the Action of Aluminium Chloride and Benzene on Mucochloric and Mucobromic Acids. By HENRY BARKER HILL, JOHN A. WIDTSOE, and FREDERICK L. DUNLAP (*Amer. Chem. J.*, 1897, **19**, 627—649).—By HENRY B. HILL (introduction).—Whereas methylic mucobromate, unlike the free acid, does not react with hydroxylamine to form an oxime (Hill and Cornelison, Abstr., 1894, i, 322), it is now found that methylic mucophenoxybromate, on the other hand, reacts no less readily than the corresponding acid. Mucochloric chloride reacts with benzene in the presence of aluminium chloride, forming a dichlorodiphenylcrotonic acid which yields diphenylacetic acid when oxidised; this can be explained by assuming the hydroxylactone constitution for mucochloric acid, when its chloride would be represented by the first of the following formulæ:



$$\left.\begin{matrix}\mathrm{CCl\cdot CHCl} \\ \| \\ \mathrm{CCl\cdot CO}\end{matrix}\right>$$

Lactone-formula.



$$\begin{matrix}\mathrm{CCl\cdot CHO} \\ \| \\ \mathrm{CCl\cdot COCl}\end{matrix}$$

Aldehyde-formula.

had the acid the aldehyde constitution, its chloride would have the second of the formulæ given, and should form an aldehyde-phenyl-ketone with benzene and aluminium chloride.

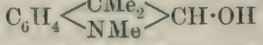
By JOHN A. WIDTSOE (p. 631).—*Methylic mucophenoxybromate*, $OPh\cdot C_4HBrO_3Me$, made by mixing the silver salt of the acid with methylic iodide, melts at 75—76°; it reacts with hydroxylamine hydrochloride, yielding a product, $OPh\cdot C_4H_2BrNO_3Me$, which can also be obtained by boiling the *silver* salt of mucophenoxybromoxime with methylic iodide. This product melts at 150—165° (at 168—170° when heated rapidly); it cannot be obtained by boiling the oxime with the alcohol and a little hydrochloric acid, but the corresponding *ethylic* derivative, which crystallises in flat, silky needles and melts at 122—124°, can be obtained in this way. When gaseous hydrogen chloride is passed into an alcoholic solution of mucophenoxybromoxime, the temperature not being allowed to rise above 20°, *mucophenoxybromoxime anhydride*, $OPh\cdot C_4HBrNO_2$, separates. This melts at 121° (at 124—126° when heated rapidly). When its alcoholic solution is boiled, with or without the addition of hydrochloric acid, it undergoes a molecular transformation into *phenoxybromomaleimide*; this melts at 144—145°, or at 148—150° when heated rapidly; it will crystallise with 1 mol. of methylic alcohol, forms a silver salt, and is converted by alkalis into phenoxybromomaleic acid, as is also the oxime anhydride.

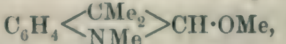
A series of analogous chlorine compounds was prepared by the same methods. *Methylic mucophenoxychlorate* melts at 59°; its oxime, identical with the methylic derivative of mucophenoxychloroxime, melts at 156—160°, or at 162—166° when heated rapidly. *Mucophenoxychloroxime anhydride* (precipitated by the addition of water to the alcoholic hydrochloric acid solution) melts at 96—98°. *Phenoxychloromaleimide* melts at 118—119°; it will crystallise with 1 mol. of methylic alcohol.

By FREDERICK L. DUNLAP (p. 641).—The action of benzene and aluminium chloride on mucochloric and mucobromic acids (which are more suitable than their respective chlorides and bromides) was studied by dissolving the acid in 5 times its weight of benzene diluted with twice its volume of carbon bisulphide, adding 1½ times its weight of aluminium chloride, heating in a reflux apparatus until the evolution of hydrogen chloride ceased, distilling off the solvent, washing the solidified residue with benzene, and recrystallising it from acetic acid. *Mucochloric chloride* boils at 100—101° under 15 mm. pressure. *Dichlorodiphenylcrotonic acid*, $C_4H_2Ph_2Cl_2O_2$, melts at 152°; the *barium* and *calcium* salts both crystallise with $2H_2O$; the acid is oxidised by alkaline permanganate to diphenylacetic acid, and reduced by sodium amalgam to *γ-diphenylbutyric* acid, which melts at 106°, and forms amorphous *silver*, *calcium*, and *barium* salts, the first of which was analysed.

Dibromodiphenylcrotonic acid melts at 146—147°; the *barium* salt, with $3H_2O$; *calcium* salt, with $2H_2O$, and the amorphous *silver* salt were prepared and analysed; the *methylic* salt obtained by heating the acid with methylic alcohol and sulphuric acid melts at 79—80°. When reduced, it yields the same products as dichlorodiphenylcrotonic acid, and when it is boiled with aqueous sodium carbonate in a reflux apparatus, the product formed is probably *diphenylbromallylene*, for it unites with bromine without evolution of hydrogen bromide, yielding a *dibromide*, $C_{15}H_{11}Br_3$, which melts between 120 and 130°. C. F. B.

Hydroxytrimethylindoline (Trimethylindolinone). By ANTONIO PICCININI (*Gazzetta*, 1897, 27, i, 473—480).—By the condensation of isobutaldehyde with phenylmethylhydrazine, Brunner (Abstr., 1896, i, 625) obtained a base of the composition $C_{11}H_{15}NO$, which yielded a trimethylindolinone on oxidation with silver nitrite; the same indolinone was prepared by Ciamician and Piccinini (this vol., i, 101) by oxidising Ferratini's (Abstr., 1893, i, 603) and Fischer's trimethyldihydroquinoline. Further, Ciamician and Piccinini (*loc. cit.*) obtained Brunner's base by reducing the indolinone with sodium and alcohol.

The author considers Brunner's base to be 2′-*hydroxy*-1′ : 3′ : 3′-trimethylindoline,  $C_6H_4{<}\substack{CMe_2\\NMe}{>}CH\cdot OH$ (compare Brunner, *loc. cit.*); it melts at 97—98°, and readily combines with methylic iodide, yielding a *methiodide*, $OH\cdot C_{10}H_{11}NMe,MeI$, which crystallises in colourless prisms melting and decomposing at 165°. This is converted by moist silver oxide into a substituted ammonium *hydroxide*, which has a strongly alkaline reaction.

On heating the methiodide with potash, 2′-*methoxy*-1′ : 3′ : 3′-*trimethylindoline*,  $C_6H_4{<}\substack{CMe_2\\NMe}{>}CH\cdot OMe$, distils and is ultimately obtained in colourless prisms which melt at 41° and sublime at the ordinary temperature; its *picrate* blackens at 150° and melts at 230°, and its *platinochloride*, $(C_{12}H_{17}NO)_2,H_2PtCl_6$, crystallises in yellow laminæ melting and undergoing decomposition at 209—210°. On heating the base with hydrogen iodide and red phosphorus at 150°, distilling the product in a current of steam, concentrating, and crystallising the residual liquor, the hydriodide of the tertiary base, $C_{10}H_{12}NMe$, is obtained (compare Ciamician and Piccinini, *loc. cit.*). The *methiodide*, $C_{12}H_{17}NO,MeI$, obtained by direct combination, crystallises in colourless, lustrous prisms melting at 183—184°; it gives a substituted ammonium *hydroxide* of strongly alkaline reaction when treated with moist silver hydroxide. W. J. P.

Researches on Organic Additive Products.—Triphenylmethane and Benzene. By Basil B. Kuriloff (*Zeit. physikal. Chem.*, 1897, **23**, 547—557).—Triphenylmethane and benzene form an additive product of the composition $CH(C_6H_5)_3,C_6H_6$, which is stated to melt at 76°. Linebarger investigated solutions of triphenylmethane in benzene, and considered that the compound was decomposed into its components above 37·5°. The author, therefore, reinvestigated the solubility relations, and obtained perfectly regular results, the curve exhibiting three portions for the equilibrium of (1) solid benzene and solution, (2) compound and solution, (3) triphenylmethane and solution. The two latter curves cut at about 74°, and at 78·2° the composition of the solution corresponds with that of the compound, and below this temperature may contain more or less benzene, that is, the curve here gives the lowering of the melting point (78·2) of the compound by the addition either of benzene or of triphenylmethane. Cryoscopic and boiling point observations gave a normal molecular weight for triphenylmethane when the formation of the compound is allowed for, so that the behaviour throughout is perfectly normal and in accord with the existence of the additive compound. L. M. J.

Action of Nitric Acid on Triphenylmethane. By E. S. Smith (*Amer. Chem. J.*, 1897, **19**, 702—703).—On one occasion, when nitric acid of sp. gr. 1·34 and then fuming nitric acid were added in indefinite quantities to triphenylmethane, the mixture allowed to remain for a short time, heated on the sand-bath for a few minutes, and then poured into water, the product consisted largely of triphenylcarbinol. Attempts to repeat the experiment have been unsuccessful.

C. F. B.

Addition of Halogen to Halogenised and Phenyl Derivatives of Ethylene. By Heinrich Biltz (*Annalen*, 1897, **296**, 263—278. Compare this vol., i, 533).—The indifference of tetraphenylethylene towards bromine is attributed by the author to the arrangement of the substituent radicles in space. Other unsaturated compounds have been therefore investigated from this point of view.

Diphenyldichlorodibromethane, $CPh_2Br\cdot CCl_2Br$, obtained from diphenyldichlorethylene and bromine, crystallises from alcohol in lustrous, refractive leaflets, melts at 120—120·5°, and may be distilled without undergoing decomposition; it develops a magenta-red coloration with a solution of potassium dichromate in concentrated sulphuric acid.

Diphenyltetrachlorethane, $CPh_2Cl\cdot CCl_3$, prepared from diphenyldichlorethylene and chlorine, crystallises from alcohol in prismatic needles melting at 85°. Alcoholic potash eliminates chlorine, and gives rise to diphenyldichlorethylene.

Phenyltrichlorethane, $CHPhCl\cdot CHCl_2$, is obtained by saturating with chlorine a solution of ω-chlorocinnamene in chloroform; it boils at 134° under a pressure of 19 mm., and at 254·5—255·5° under atmospheric pressure, a part undergoing decomposition. The sp. gr. = 1·3622 at 15°/4°, and the refractive index $n_D = 1{\cdot}5652$, whence the molecular refraction $M = 50{\cdot}03$.

Phenyldichlorethylene, $CHPh{:}CCl_2$, prepared from phenyltrichlorethane and alcoholic potash, boils at 103·5°, 123°, and 225° under pressures of 15 mm., 32 mm., and 774 mm. respectively; it has a sp. gr. = 1·2651 at 15°/4°, the refractive index $n_D = 1{\cdot}5899$, and the molecular refraction $M = 46{\cdot}09$.

Phenyltetrachlorethane, $CHPhCl\cdot CCl_3$, is formed from the foregoing substance when chlorine is passed into the solution in chloroform; it is colourless and odourless, and boils at 138—139°, 148°, and 267—268° under pressures of 12 mm., 21 mm., and 773 mm. respectively. The substance has a sp. gr. = 1·453 at 15°/4°, and the refractive index $n_D = 1{\cdot}5718$, whence the molecular refraction $M = 55{\cdot}16$.

Phenyltrichlorethylene, $CClPh{:}CCl_2$, is prepared by the action of alcoholic potash on phenyltetrachlorethane, and boils at 121°, 130°, and 235° under pressures of 23 mm., 31 mm., and 751 mm. respectively; the sp. gr. = 1·376 at 15°/4°, the refractive index $n_D = 1{\cdot}5861$, and the molecular refraction $M = 50{\cdot}54$.

Phenylpentachlorethane, $CCl_2Ph\cdot CCl_3$, is obtained by passing chlorine into a solution of the foregoing compound in chloroform. It separates from alcohol or glacial acetic acid in lustrous, rhombic crystals, melts at 37—38°, and boils at 178—179° under a pressure of 34 mm. *Nitrophenylpentachlorethane*, $NO_2\cdot C_6H_4\cdot CCl_2\cdot CCl_3$, is produced by the action of fuming nitric acid; it separates from alcohol in colourless, monoclinic crystals, and melts at 114°.

Phenyl-ω-chloro-αω-dibromethane, $CHPhBr\cdot CHClBr$, is prepared from ω-chlorocinnamene by the action of bromine, and boils at 165° under a pressure of 26 mm.; it crystallises from dilute alcohol in colourless, triclinic needles, and melts at 32°.

Phenyl-ωω-dichloro-αω-dibromethane, $CHPhBr\cdot CCl_2Br$, is obtained from phenyldichlorethylene and undiluted bromine; it is a viscous, yellowish oil, and distils at 175° under a pressure of 24 mm., evolving bromine.

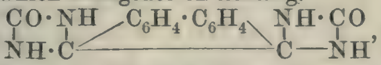
Phenyl-αωω-trichloro-αω-dibromethane, $CPhClBr\cdot CCl_2Br$, produced by the action of undiluted bromine on phenyltrichlorethylene, separates from alcohol in rhombic crystals melting at 47—48°.

Phenyldichlorethane, $CHPhCl\cdot CH_2Cl$, has not been previously obtained in the purified state. It boils at 114·5—115·5° under a pressure of 15 mm., and scarcely undergoes change when distilled under the ordinary pressure at 233—234°; its sp. gr. = 1·240 at 15°/4°, and the refractive index $n_D = 1{\cdot}554$, whence the molecular refraction $M = 45{\cdot}21$.

Consideration of the foregoing compounds shows that, in the case of phenylethane derivatives, the atomic refraction of chlorine increases with the number of halogen atoms; in the phenylethylene series, however, this constant decreases as substitution becomes more complete. M. O. F.

Action of Carbamide on Quinones. By SIRO GRIMALDI (*Gazzetta*, 1897, **27**, i, 228—246. Compare Abstr., 1895, i, 425).—After boiling phenanthraquinone with carbamide in acetic acid solution in a reflux apparatus for 24 hours, and cooling the solution, a *monoureine*, $C_6H_4\left<\begin{matrix}C_6H_4\\CO\end{matrix}\right>C\left<\begin{matrix}NH\\NH\end{matrix}\right>CO$, separates; it crystallises in white needles melting at 299°, and its solution in dilute acetic acid is fluorescent. On boiling with hydroxylamine acetate in acetic acid solution, it gives a crystalline *oxime*, $CO\left<\begin{matrix}NH\\NH\end{matrix}\right>C\left<\begin{matrix}C(N\cdot OH)\\C_6H_4\end{matrix}\right>C_6H_4$; this melts at 200—202°, and is hydrolysed by boiling with dilute hydrochloric acid. A *dinitro*-derivative, $C_6H_4\left<\begin{matrix}C_6H_4\\CO\end{matrix}\right>C\left<\begin{matrix}N(NO_2)\\N(NO_2)\end{matrix}\right>CO$, is obtained on heating the ureine with nitric acid in sealed tubes; it crystallises in yellow needles which deflagrate on heating.

The *diureine*,

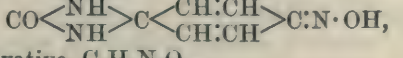


$\begin{matrix}CO\cdot NH & C_6H_4\cdot C_6H_4 & NH\cdot CO\\ NH\cdot C & & C - NH\end{matrix}$

prepared by heating phenanthraquinone with carbamide in an oil bath at 250°, is an amorphous, white powder which decomposes on heating. When treated with a mixture of sulphuric and fuming nitric acids, it yields a *dinitro*-derivative, $C_{16}H_{10}N_6O_6$; this crystallises in yellow needles which deflagrate at 300°, and by analogy with diacetyldiphenylacetylenediureine (Angeli, Abstr., 1890, 1290) and dinitrodimethylacetylenediureine (Franchimont and Klobbie, Abstr., 1889, 125) must contain the group $>C\left<\begin{matrix}N(NO_2)\\N(NO_2)\end{matrix}\right>CO$.

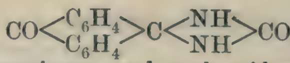
β-Naphthaquinonemonoureine, $O:C_{10}H_6\left<\begin{matrix}NH\\NH\end{matrix}\right>CO$, is prepared by boiling β-naphthaquinone with carbamide in acetic acid solution; it melts at 162—163°, and yields a crystalline *oxime*, $C_{11}H_9N_3O_2$, and a *dinitro*-derivative, $O:C_{10}H_6\left<\begin{matrix}N(NO_2)\\N(NO_2)\end{matrix}\right>CO$; the latter crystallises in yellow needles which deflagrate when strongly heated. A white *diureine*, $CO\left<\begin{matrix}NH\\NH\end{matrix}\right>C_{10}H_6\left<\begin{matrix}NH\\NH\end{matrix}\right>CO$, is obtained by heating a mixture of β-naphthaquinone and carbamide at 200° in an oil bath; it yields a *dinitro*-compound, $CO\left<\begin{matrix}NH\\NH\end{matrix}\right>C_{10}H_6\left<\begin{matrix}N(NO_2)\\N(NO_2)\end{matrix}\right>CO$, crystallising in yellow needles which deflagrate on heating.

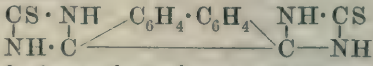
Quinonemonoureine, $CO\left<\begin{matrix}CH:CH\\CH:CH\end{matrix}\right>C\left<\begin{matrix}NH\\NH\end{matrix}\right>CO$, is formed on boiling quinone with carbamide in acetic acid solution, but is best prepared by heating quinone with carbamide for 8—10 hours at 140—150° in a sealed tube; it crystallises in yellow needles which do not melt at 320°, and yields a crystalline oxime,



$$CO\left<\begin{matrix}NH\\NH\end{matrix}\right>C\left<\begin{matrix}CH:CH\\CH:CH\end{matrix}\right>C:N\cdot OH,$$

and a *dinitro*-derivative, $C_7H_4N_4O_6$.

Anthraquinonemonoureine,  $CO\Big<\begin{smallmatrix}C_6H_4\\C_6H_4\end{smallmatrix}\Big>C\Big<\begin{smallmatrix}NH\\NH\end{smallmatrix}\Big>CO$, prepared by heating a mixture of anthraquinone and carbamide at 300°, is an amorphous substance which melts at above 320° with decomposition; it yields a crystalline *oxime*, $C_{15}H_{11}N_3O_2$, and a *dinitro*-derivative, $C_{15}H_8N_4O_6$, which crystallises in yellow needles. The author was unable to prepare the corresponding diureine.

Phenanthraquinone dithiodiureine, , is obtained by heating a mixture of phenanthraquinone and thiocarbamide on an oil bath at 210°, and is purified by precipitating its sulphuric acid solution with water; it forms a crystalline, red powder which melts and decomposes at above 320°. W. J. P.

Nitro-compounds of Anthragallol. By Max Bamberger and Fritz Böck (*Monatsh.*, 1897, 18, 283—301).—Dry anthragallol, purified by removing the admixed benzoic acid by sublimation and recrystallising the residue from alcohol, is added in small portions at a time to fuming nitric acid, taking care that the temperature never rises above −15°. As the reaction proceeds, *ψ-nitroanthragallol* separates in fine, dark-red crystals; these are collected as rapidly as possible, purified by washing with cooled water to which a little hydrochloric acid has been added, and dried in a vacuum over sulphuric acid. In the dry condition, it is quite stable, and dissolves without change in alcohol, ethylic acetate, chloroform, benzene, and xylene, forming a yellow to red solution, and in alkalis with a green colour. The same nitro-derivative is obtained when anthragallol is exposed to the fumes of nitric acid.

α-Nitroanthragallol is prepared by boiling the ψ-nitro-compound with water, when the violet colour of the solution disappears, and a yellowish-brown substance separates, which is purified by recrystallisation, first from alcohol, and then from a mixture of alcohol and light petroleum. During the reaction, gas is given off consisting of a mixture of carbonic anhydride, nitric oxide, and nitrogen. α-Nitroanthragallol, which crystallises from alcohol in beautiful, golden-brown, feathery needles, melts at 224°, is easily soluble in ether, benzene, and chloroform, but insoluble in water and light petroleum. It dissolves in alkalis with a green, and in concentrated sulphuric acid with a red to brown, coloration. On oxidation with dilute nitric acid, phthalic acid is produced, thus showing that the nitro-group is contained in the same ring as the three hydroxyl groups.

When α-nitroanthragallol is covered with ammonia solution, and hydrogen sulphide is passed through the liquid, the green solution changes to brown and *amido-anthragallol* separates; this crystallises from ethylic acetate in groups of prismatic needles, is soluble in water, alcohol, ethylic acetate, and benzene, forming a red solution, and in alkalis with a dark bluish-red colour. If an acid is added to the solution, it becomes bright red, and a reddish-brown precipitate is formed.

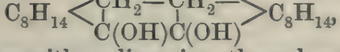
β-Nitroanthragallol.—When ψ-nitroanthragallol is boiled with a small quantity of absolute alcohol, it dissolves with evolution of gas, and, on cooling, golden-yellow needles separate, which can be recrystallised from alcohol; the gas consists of a mixture of ethylic nitrite, carbonic anhydride, oxygen, and nitrogen. On oxidation, phthalic acid is obtained, showing that, in this compound also, the nitro-group must be attached to the same ring as the hydroxyl groups. An amido-anthragallol, which crystallises from ethylic acetate in small needles having a feeble greenish-metallic lustre, can be prepared from β-nitro-anthragallol by the method described above.

Tribenzoylanthragallol, obtained by the action of benzoic chloride on anthragallol, crystallises from ethylic acetate in small, yellow plates melting at 207°. By the action of fuming nitric acid, it is converted into a *nitrobenzoylanthragallol*, which crystallises from glacial acetic acid in beautiful golden-yellow plates melting at 209°.

The probable constitution of the various nitro-compounds is discussed and an account of their absorption spectra given. A. W. C.

Action of Sodium on Camphor. By Giuseppe Oddo (*Gazzetta*, 1897, **27**, i, 203—207).—Baubigny (*Ann. chim. phys.*, 1870, [iv], **19**, 121) only succeeded in preparing a monosodio-derivative of camphor, but Brühl (Abstr., 1892, 200) obtained evidence of the formation of disodiocamphor during the preparation of ethylcamphor. Since the author has previously shown (see following abstract) that the sodio-derivative of dicamphor is readily oxidised by atmospheric oxygen to dicamphanhexane-1:4-dione, if camphor yields a disodio-derivative, this should be oxidised by atmospheric oxygen to sodiodicamphor. The author finds that, on treating camphor with sodium in toluene solution, the product contains small quantities of the dicamphor derivatives which he has previously prepared from dicamphor; he therefore concludes that camphor, like benzophenone and some other ketones, does yield a disodio-derivative.

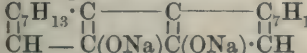
The author confirms Beckmann's observation (Abstr., 1894, i, 614) respecting the formation of camphopinacone (αα-dicamphandiol),



$$C_8H_{14}<\begin{array}{l}CH_2-CH_2-\\ C(OH)C(OH)\end{array}>C_8H_{14},$$

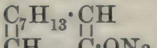
on treating camphor with sodium in ethereal solution. Unlike the ββ-dicamphor compounds, this substance is not converted into camphor by prolonged boiling with sodium in toluene solution. W. J. P.

Action of Sodium on Dicamphor and Dicamphanhexane-1:4-dione. By Giuseppe Oddo (*Gazzetta*, 1897, **27**, i, 197—202).—Sodium acts on ββ-dicamphor and on dicamphanhexane-1:4-dione in toluene solution, with formation of a mixture of these two substances with camphor, borneol, and the mixture of acids obtained by treating bromocamphor with sodium (this vol., i, 430). The dicamphanhexanedione is thereby converted into sodiodicamphor,



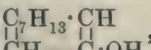
$$\begin{array}{l}C_7H_{13}\cdot C \text{———} C \text{———} C_7H_{13}\\ CH - C(ONa)C(ONa)\cdot CH\end{array},$$

and the dicamphor is converted into sodiocamphor,



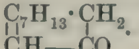
$$\begin{array}{l}C_7H_{13}\cdot CH\\ CH - C\cdot ONa\end{array};$$

this, on hydrolysis, yields a labile modification of camphor of the constitution



$$\begin{array}{l}C_7H_{13}\cdot CH\\ CH - C\cdot OH\end{array},$$

which then changes into the stable form,



$$\begin{array}{l}C_7H_{13}\cdot CH_2\\ CH - CO\end{array}.$$

The author considers that he has thus demonstrated the existence of the group $-CH_2\cdot CO\cdot CH=$ in camphor, and therefore concludes that the constitutions which Kekulé and Bredt have assigned to camphor are erroneous. W. J. P.

Pinene; a Correction. By ALBERT REYCHLER. (*Bull. Soc. Chim.*, 1896, [iii], 15, 969—970).—The author modifies his view of the changes involved in the conversion of pinene into camphene (compare Abstr., 1896, i, 313 and 620). A. C. C.

Essence of Bitter Fennel. By E. TARDY (*J. Pharm.*, 1897, [vi], 6, 98—102).—The author has found the following substances in the essence of French-grown, bitter fennel, supplied by the Grasse Distillery; a bivalent, dextrogyrate terebenthene, phellandrene, cymene, fenchone, estragol, anethoil, anisaldehyde, anisic acetone,

$$MeO\cdot C_6H_4\cdot CH_2\cdot COMe,$$

identical with the substance previously obtained from essence of anise, anisic acid, and a crystalline compound, $C_{13}H_{14}O_2$, melting at 213°.

J. J. S

Active Principles of some Aroideæ. By Mdlle. J. CHAULIAGUET, ALEXANDRE HÉBERT, and F. HEIM (*Compt. rend.*, 1897, **124**, 1368—1370).—Experiments were made with *Arum maculatum*, *A. italicum*, and *Arisarum vulgare*. The products obtained were (1) a glucoside having all the general properties of a saponin, and existing in all parts of the plant, but more especially in the root nodules, from which it seems to migrate in the spring to the subaërial parts of the plant. Its poisonous effects are similar to those of the sapotoxins, but are feebler, and it does not destroy the irritability of nerves and muscular striæ, and has scarcely any effect on the heart. (2) A very volatile, unstable, brown, liquid alkaloid, only slightly soluble in water, but soluble in all ordinary organic solvents. Both the base and its hydrochloride, which crystallises in very deliquescent needles, have a strong odour of mice. All its general properties are identical with those of conicine, but its poisonous properties are less active; it is probably an isomeride or a higher homologue. The existence in the *Aroideæ* of an alkaloid, or a close relation of an alkaloid, characteristic of such a very different natural order as the *Umbelliferæ*, is a point of considerable interest. A similar alkaloid also exists, together with saponin, in *Caladium bulbosum* and *Amorphophallus Rivieri*.

No evidence could be obtained of the existence of hydrocyanic acid either free or combined, in any of the *Aroideæ* examined.

C. H. B.

Spectra of Chlorophylls. By ALEXANDRE LÉON ÉTARD (*Compt. rend.*, 1897, **124**, 1351—1354).—When comparing the spectra of chlorophylls, it is essential to examine solutions of known concentration in a specified solvent and in layers of definite thickness, and the comparison is greatly facilitated by using the ordinary comparison prism. Chlorophyll extracted from perennial rye-grass (*Lolium perenne*) by carbon bisulphide and carefully freed from fats, alkaloids, free acids, &c., was examined in a carbon bisulphide solution containing one part in 10,000 and in a layer 150 mm. deep. It showed bands at λ 729—635; 635—598; 580—564;

559—549, and 528—507, the mean axes being approximately 682, 616·5, 572, 554, and 517 respectively. With only one part in 50,000, the bands at 517 and 616·5 disappear; the band 559—549 has a definite axis 549, whilst 580—564 becomes very narrow and has a definite axis 564. With one part in 100,000, the band 564 disappears, and 549 becomes practically a line, whilst with one part in 500,000 the only visible band is that at 681·5.

The principal band at 729—635 is continuous with one part in 10,000, but with one part in 50,000 it splits up into three bands; one, slender at 713—704, with its axis at 708·5; a second, somewhat stronger with its axis at 681·5, and a third, weaker at 659—650, with its axis at 654·5. The band at 681·5 is visible when the solution contains only one part in 500,000.

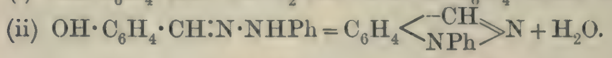
It follows that it is impossible to see all the absorption bands at once, since some disappear at the degree of dilution necessary to make the others distinguishable.

The method of successive dilutions is of great value in distinguishing chlorophylls from one another, and also in determining the exact effect of reagents, such as the splitting up of the principal band into three by the action of weak potassium hydroxide solution. C. H. B.

Coleopterin, a Pigment in the Elytræ of some Coleoptera. By ARTHUR BOWER GRIFFITHS (*Compt. rend.*, 1897, **124**, 1460—1461).—The elytræ of *Pyrochroa coccinea*, *Lina populi*, and *Coccinella septempunctata* contain a red, amorphous pigment soluble in alcohol, ether, carbon bisulphide, and acetic acid. It contains C, 45·86; H, 2·74, and N, 7·7 per cent., which corresponds with the formula $C_7H_5NO_5$. It is a lutein or a lipochrome, and the author gives it provisionally the name *coleopterin*. Its solutions show no definite absorption spectrum, but they are decolorised when exposed to light. C. H. B.

Phenylisindazole. By HENRI EUGÈNE CAUSSE (*Compt. rend.*, 1897, **124**, 505—506).—The product of the interaction of salicylaldehyde and phenylhydrazine melting at 142° has hitherto been regarded as a hydrazone, but the author finds that its composition and properties are those of a member of the isindazole group. It is prepared by adding to a well-cooled solution of phenylhydrazine (30 grams) and acetic anhydride (10 grams) in alcohol (150 c.c.) a solution of orthosalicylaldehyde (30 grams) also dissolved in alcohol (about 100 c.c.). The crystals which separate on cooling, after being dried and recrystallised from alcohol, are obtained as colourless, prismatic needles melting at 142° without undergoing decomposition, and having the formula $C_{13}H_{10}N_2$. They are insoluble in water, and only slightly soluble in alcohol, ether, and benzene in the cold, but are somewhat more so in these liquids on warming. Caustic alkalis are without action on the substance, ferric chloride gives no coloration, and Fehling's solution is not reduced. Heated in sealed tubes at 100° with acetic anhydride or benzoic anhydride, brown liquids are obtained from which the original substance can be recovered by treatment with caustic soda. Alkylic iodides are without action, and no nitroso-derivative is obtained by the action of nitrous anhydride. The production of phenylisindazole can be represented by means of the two following equations.

(i) $OH\cdot C_6H_4\cdot COH + NH_2\cdot NHPh = OH\cdot C_6H_4\cdot CH{:}N\cdot NHPh + H_2O$,



(ii) $OH\cdot C_6H_4\cdot CH{:}N\cdot NHPh = C_6H_4{<}\substack{-CH\\ NPh}{>}N + H_2O$.

Parahydroxybenzaldehyde, when submitted to the same treatment as the ortho-derivative, does not yield any crystalline product, but in aqueous solution a crystalline substance is obtained melting at 179°, the composition of which is being studied by the author. A. C. C.

The Pyrazole Series. By LUIGI BALBIANO (*Gazzetta*, 1897, **27**, i, 415).—The author replies briefly to Claisen's criticism (this vol., i, 440) of the work of Balbiano and Severini (Abstr., 1893, i, 673), and states his intention of repeating the work in question. W. J. P.

Metallic Compounds of Pyridine and the Electrolysis of Pyridine. By FRITZ REITZENSTEIN (*Zeit. anorg. Chem.*, 1897, **15**, 192—193).—The author is engaged on the study of the hydrates, ammonia and pyridine compounds of bivalent metals. He gives a list of the metallic compounds of pyridine which he has prepared. These will be described later. Pincussohn, in his recent paper (this vol., i, 540), has evidently overlooked the author's work (*Annalen*, 1894, **282**, 270—280 ; *Zeit. anorg. Chem.*, 1896, **11**, 254—263).

E. C. R.

"Loretin"; Metiodorthohydroxyquinolineanasulphonic Acid. By ADOLF CLAUS and SIGISMUND BAUMANN (*J. pr. Chem.*, **55**, 457—480).—Several alkali earth salts of metiodorthohydroxyquinoline-anasulphonic acid, known as "loretin," are described.

Neutral calcium loretate, $(OH\cdot C_9NH_4I\cdot SO_3)_2Ca + 2\frac{1}{3}H_2O$ [$I : OH : SO_3 = 3 : 2 : 5$], crystallises in fiery red prisms, which lose $\frac{1}{3}H_2O$ at 100° without change of colour, and the other $2H_2O$ at 130°, changing to light yellow. Its aqueous solution is decomposed by sunlight at 60—70°, iodine being liberated. The *basic salt* is an anhydrous, cream-coloured compound crystallising in needles. *Neutral strontium loretate* forms orange-red prisms containing $1H_2O$, and the *basic salt* slender anhydrous needles. *Neutral barium loretate* consists of orange-red needles containing $2\frac{1}{2}H_2O$, the *basic salt* forming slender needles of a greenish-yellow colour, and containing $1H_2O$. *Neutral magnesium loretate*, best produced by treating "loretin" with magnesium carbonate, crystallises in prisms with $7H_2O$; the *basic salt* crystallises with $5H_2O$.

Two acids are produced by the decomposition of sodium loretate in boiling water. The first is evidently orthohydroxyquinolineanasulphonic acid, whilst the second, which is more soluble and can be separated from it by fractional crystallisation, consists of dark red prisms softening at 285°, and is probably an anhydrous compound of 1 mol. orthohydroxyquinolineanasulphonic acid with 1 mol. of 1 : 2-dihydroxyquinolineanasulphonic acid, the *neutral barium* salt consists of yellow, transparent plates, whilst the *acid salt* forms fiery red, glistening needles containing $9H_2O$. and the *basic salt* greenish-yellow crystals insoluble in cold water. J. F. T.

Derivatives of Isonarcotine: Hydrodicotarnine, a New Base. By E. BANDOW (*Ber.*, 1897, **30**, 1745—1749).—Attempts to resolve isonarcotine into optical components by means of tartaric and racemic acids have, hitherto, been fruitless.

Hydrogen isonarcotine d-*tartrate* contains $3\frac{1}{2}H_2O$, and forms long, colourless needles melting at 180°; *hydrogen isonarcotine* l-*tartrate* also contains $3\frac{1}{2}H_2O$, and crystallises in white plates melting at the same temperature as the foregoing salt. *Hydrogen isonarcotine racemate* is almost insoluble in cold water, and crystallises in small, white needles.

Isonarcotine *ethiodide* is readily soluble in water and alcohol, and forms small, white crystals melting at 183°; the *ethochloride* is amorphous, and yields an orange *platinochloride.* The *ethylhydroxide* is very deliquescent, and with concentrated sulphuric acid does not give the red coloration characteristic of the original base. Although an aqueous solution of narcotine ethylhydroxide undergoes spontaneous conversion into ψ-homonarceine, neither the ethylhydroxide nor the methylhydroxide of isonarcotine exhibits the corresponding change, the unaltered substances being recovered on evaporating the aqueous solutions. Isonarcotine *methiodide* forms small, white needles, and melts at 212°; the *platinochloride* of the methochloride has been analysed; the *methylhydroxide* is very hygroscopic.

Hydrodicotarnine, $C_{24}H_{28}N_2O_6$, is prepared by heating hydrocotarnine with 73 per cent. sulphuric acid for half an hour at about 80°; it is also produced when the base is dissolved in cold 82 per cent. sulphuric acid, when the temperature rises spontaneously to 60°. It is insoluble in ammonia, and somewhat sparingly soluble in benzene, but dissolves readily in alcohol or chloroform; it crystallises in small, bright yellow needles, and melts at 211°. The *hydrobromide* forms white needles melting at 218—220°, and the *hydriodide* is yellowish and melts at 227—229°; the *platinochloride* is orange-yellow.

A table comparing the properties and derivatives of hydrodicotarnine with those of the closely related cotarnine and hydrocotarnine is included in the paper. M. O. F.

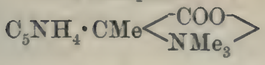
Pilocarpine and Pilocarpidine. By AUGUSTE PETIT and MAX POLONOWSKY (*J. Pharm.*, 1897, [vi], **5**, 370—375, 430—437, and 475—483. Compare Hardy and Calmels, *Compt. rend.*, **102**, 1116, 1251, and 1562).—Paul and Cownley have already pointed out (*Pharm. J. Trans.*, July and November, 1896) that different specimens of commercial pilocarpine and its derivatives differ largely, not only in their physical properties, but also in their physiological action. The authors have therefore undertaken the study of the two alkaloids, pilocarpine and pilocarpidine, and of their derivatives. These two compounds are easily separated from the other bases which occur in jaborandi leaves, since they both combine with alkali hydroxides, yielding compounds which are insoluble in chloroform or ether. The best method for separating the two is by fractional crystallisation of their hydrochlorides from alcohol. A simple method for converting pilocarpine into pilocarpidine is to heat the base or one of its salts with an alcoholic solution of sodium ethoxide on a water bath.

The following table gives a *résumé* of the chief properties of the two alkaloids and their salts :—

	Pilocarpine.	Pilocarpidine.
Free base	Thick syrup, $[\alpha]_D$ in aqueous solution $= +106°$; in the presence of soda, $[\alpha]_D = +23·8°$.	Deliquescent prisms, $[\alpha]_D = +50°$; in presence of soda, $[\alpha]_D = -3°$.
Nitrate	Prisms. Soluble in 7 parts of water at 18°, and in 146 parts of alcohol (95 per cent.) at 18°. Melting point 177—178°. $[\alpha]_D = +82·2°$.	Plates. Soluble in 8 parts of water, or 135 parts of alcohol. Melting point 158°. $[\alpha]_D = +38·5°$.
Hydrochloride	Anhydrous prisms. Soluble in 0·4 part of water, or in 10 parts of alcohol. Melting point 200°. $[\alpha]_D = +91°$.	Flakes containing water of crystallisation. Soluble in 0·27 part of water, or in 2 parts of alcohol. Melting point of the hydrated salt = 124°, and of the anhydrous salt = 161°. $[\alpha]_D = +37·3°$.
Hydrobromide	Prisms. Melting point 178°. $[\alpha]_D = +76°$.	Needles. Melting point 143°. $[\alpha]_D = +32·6°$.
Salicylate	Melting point 120°. $[\alpha]_D = +62·5°$.	Melting point 99°. $[\alpha]_D = +30°$.
Picrate	Hard needles. Melting point 159—160°.	Silky needles. Melting point 160—161°.
Sulphate	Small needles. Melting point 120°. $[\alpha]_D = +86°$.	Not been prepared.
Acid aurochloride	Yellow needles melting at 100°, or when anhydrous at 130°.	Anhydrous needles. Melting point 160°.
Modified aurochloride	Melting point 167°.	Melting point 190°.
Iodomethoxide	Not been prepared.	Prisms. Melting point 108°. $[\alpha]_D = +26°$.

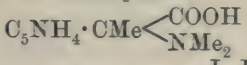
The authors find that the impurities in commercial pilocarpine salts are the corresponding pilocarpidine compounds; in the case of the nitrate, the latter sometimes amounts to 50 per cent. The authors also think that the pilocarpidine exists ready formed in the plant, and is not produced from pilocarpine during the process of extraction (compare Hardy and Calmels). The pilocarpic and pilocarpidic acids which Hardy and Calmels believed to be hypothetical compounds, of which pilocarpine and pilocarpidine might be regarded as the anhydrides, have actually been obtained by the authors. Sodium pilocarpate is formed when pilocarpine dissolves in caustic soda; this may be transformed into the barium salt, and when the latter is treated with the requisite quantity of sulphuric acid, and the filtrate allowed to evaporate spontaneously, free *pilocarpic acid* is obtained in the form of a syrup. It is readily soluble in water or alcohol, but insoluble in ether, chloroform, or benzene, $[\alpha]_D = +23·8°$. It gradually loses water when heated, and more rapidly on the addition of acids, even if dilute, being reconverted into pilocarpine. *Pilocarpidic acid* resembles the above acid in all its properties except that it is lævogyrate. The following constitutional formulæ are suggested for the two alkaloids:—

Pilocarpine.



$C_5NH_4\cdot CMe<\begin{matrix}COO-\\NMe_3\end{matrix}>$

Pilocarpidine.



$C_5NH_4\cdot CMe<\begin{matrix}COOH\\NMe_2\end{matrix}$

J. J. S.

Isomerism of Pilocarpine and Pilocarpidine. By AUGUSTE PETIT and MAX POLONOWSKY (*J. Pharm.*, 1897, [vi], **6**, 8—11. Compare preceding abstract).—The authors now show that pilocarpine is isomeric with pilocarpidine, and that it cannot have the constitution suggested by Hardy and Calmels, since, when transformed into pilocarpidine, it yields no methylic alcohol. The transformation may be brought about by boiling pilocarpine or one of its salts with sodium ethoxide or with an aqueous solution of sodium hydroxide. Pilocarpine hydrochloride is also quantitatively converted into pilocarpidine hydrochloride when heated for a few minutes just above its melting point.

Pilocarpine platinochloride, $C_{11}H_{16}N_2O_2,H_2PtCl_6$, crystallises from boiling water in large, orange plates. 0·8 part of the salt dissolves in 100 parts of water at 23°. Its melting point is 213°.

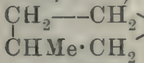
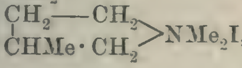
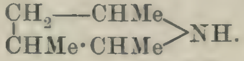
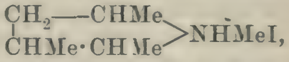
Pilocarpidine platinochloride is much less soluble in boiling water than its isomeride, but resembles it in crystalline form; it melts at 222—224°. Hardy and Calmels describe this compound as containing water of crystallisation and as melting at 130°, whilst Merck gives the melting point as 183—190°. J. J. S.

Two New Alkaloids isolated from a Species of Jaborandi. By AUGUSTE PETIT and MAX POLONOWSKY (*J. Pharm.*, 1897, [vi], **5**, 369—370). — The authors have isolated two new alkaloids from Holme's *Aracati Jaborandi*, *Pilocarpus spicatus*. The leaves are extracted in the usual way, and the mixture of bases obtained converted into nitrates. The mixed nitrates are then treated with sodium hydroxide and extracted with chloroform. After evaporating the chloroform, an alkaloid, *ψ-jaborine*, is obtained as a colourless oil with strongly alkaline properties and readily soluble in water, alcohol, or chloroform. It is optically inactive, and yields a *nitrate* which crystallises in large, thin plates melting at 158°, and a *hydrochloride* which forms small, hard prisms and melts at 222°. The second alkaloid, *ψ-pilocarpine*, has very much the same properties as pilocarpine, except that it is optically inactive. Its *nitrate* crystallises in small needles melting at 142°, and is more readily soluble in alcohol than ψ-jaborine nitrate. Its *hydrochloride* forms small prisms sparingly soluble in alcohol or water, and melts at 198—199°. J. J. S.

New Reaction of Eserine. By A. J. FERREIRA DA SILVA (*Zeit. anal. Chem.*, 1897, **36**, 540; from *Pharm. Zeit. für Russland*, **32**, 629).—Eserine and its salts, dissolved in fuming nitric acid, give yellow solutions which, when warmed on the water bath, become darker and leave a green residue. The latter dissolves with a green colour in water and strong alcohol; dissolved in dilute nitric acid, the solution fluoresces greenish-yellow by transmitted light, blood-red by reflected light. The absorption spectrum differs from those of physostygmine and rubreserine. M. J. S.

Action of Iodine on Proteids. By E. LÉPINOIS (*J. Pharm.*, 1897, [vi], 5, 561—566).—A solution of iodine is added to milk until, at the end of 24 hours, free iodine can still be detected by agitation with chloroform. At the end of this time, the mixture is poured into an equal volume of water containing a small quantity of acetic acid, and the brown coagulum thus obtained is washed first with water by decantation, and then with dilute caustic soda, which dissolves the iodocasein. The filtered liquid is precipitated by means of acetic acid, the operations of solution and precipitation being repeated five or six times, when the *iodocasein* is obtained in a pure form. After washing with water, alcohol, and ether, and drying, it is obtained as a slightly yellow, amorphous powder containing 21·6 per cent. of iodine and 14·15 per cent. of nitrogen. When heated, it melts and then carbonises. It is readily soluble in acetic acid, and in potassium, sodium, and ammonium hydroxides or carbonates, but is insoluble in alcohol, ether, chloroform, and water. None of these solvents withdraw any of its iodine, and the percentage of iodine remains constant after repeated solution and precipitation. The therapeutic properties of the substance are being examined. J. J. S.

Organic Chemistry.

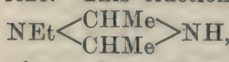
Synthesis and Constitution of Isoprene. By WILHELM EULER (*Ber.*, 1897, **30**, 1989—1991).—3-Methylpyrrolidine has been subjected to the same series of reactions as Ciamician and Magnaghi (Abstr., 1885, 1242) performed with pyrrolidine itself. 3-Methylpyrrolidine,  $\begin{matrix}CH_2\text{—}CH_2\\ CHMe\cdot CH_2\end{matrix}>NH$, if treated with methylic iodide, yields a compound,  $\begin{matrix}CH_2\text{—}CH_2\\ CHMe\cdot CH_2\end{matrix}>NMe_2I$, which, when distilled with potash, yields 2 : 3 : 5-trimethylpyrrolidine,  $\begin{matrix}CH_2\text{—}CHMe\\ CHMe\cdot CHMe\end{matrix}>NH$. This again unites with methylic iodide, yielding a compound,  $\begin{matrix}CH_2\text{—}CHMe\\ CHMe\cdot CHMe\end{matrix}>NHMeI$, which, when distilled with potash, yields trimethylamine and an unsaturated hydrocarbon, $CH_2{:}CH\cdot CMe{:}CH_2$; the latter boils at 33—39°, and forms, with hypochlorous acid, a product, $C_5H_{10}O_2Cl_2$, melting at 80—81°, and identical with that obtained by the action of the same acid on isoprene (Mokiewsky, *Chem. Zeit.*, 1895, No. 101). It must therefore be isoprene, to which, then, the above constitution must be assigned. C. F. B.

Compounds of Mercuric Cyanide with Metallic Haloids. By RAOUL VARET (*Ann. Chim. Phys.*, 1896, [vii], **8**, 240—288, and 437—438).—The first section of this paper deals with the thermochemistry of the compounds of mercuric cyanide with a number of metallic haloids. In the first chapter of this section, the heats of formation of compounds of mercuric cyanide with the iodides of sodium, ammonium, lithium, barium, strontium, calcium, magnesium, and cadmium are given (Abstr., 1896, ii, 148); in the second chapter, the heats of formation of the corresponding bromocyanides (Abstr., 1896, ii, 88), and in the third the heats of formation of the corresponding chlorocyanides (Abstr., 1896, i, 3). In the second section of this paper, the author describes experiments made with the object of distinguishing cyanogen combined with mercury from cyanogen combined with the other metals above referred to, in order that some light might be thrown upon the constitution of the double salts in question. The third section deals with the application of these methods and the conclusions arrived at (Abstr., *loc. cit.*). A. C. C.

Magnesium Methylic Carbonate and Sulphite. By EMERICH SZARVASY (*Ber.*, 1897, **30**, 1836—1838).—If magnesium methoxide (this vol., i, 309) is suspended or dissolved in methylic alcohol, and carbonic anhydride passed in, a clear solution is obtained, and after the alcohol has been evaporated *magnesium methylic carbonate*, $(OMe\cdot COO)_2Mg$, remains as a white, amorphous powder. When a methyl alcoholic solution of this substance is treated with a few drops of water, a gelatinous precipitate forms; this redissolves when more water is added, but the solution, when boiled, deposits magnesium carbonate, and is found to contain methylic alcohol. Acids decompose the compound with evolution of carbonic anhydride, a magnesium salt and methylic alcohol being formed in addition.

If sulphurous, instead of carbonic, anhydride is employed, or if sulphurous anhydride is passed into the solution of the methylic carbonate in methylic alcohol, *magnesium methylic sulphite*, $(OMe\cdot SOO)_2Mg$, is formed. This is exactly analogous to the carbonate in its properties and reactions. C. F. B.

Separation of Methylamines. By MARCEL DELÉPINE (*Ann. Chim. Phys.*, 1896, [vii], 8, 439—465).—A new method is described for the separation in a state of purity of the methylamines (Abstr., 1896, i, 519), and the properties of some of their salts and derivatives are given (Abstr., 1896, i, 588). Trimethylamine hydriodide crystallises in large, colourless plates melting at about 260° to a red liquid, and is not deliquescent. Methylamine may be conveniently separated as the bismuthoiodide described by Kraut, the base being obtained from it by treatment with caustic alkalis. A. C. C.

Action of Dichlorethylamine on Ethylamine. By EDUARD LIPPMANN and CARL REGENSDORFER (*Ber.*, 1897, 30, 2053—2057).—Dichlorethylamine prepared by Tscherniak's method (*Ber.*, 1876, 9, 146) was added drop by drop to thoroughly dried ethylamine placed in a freezing mixture of ice and salt. At the end of 24 hours, the clear liquid was decanted from the crystals of ethylamine hydrochloride, the latter being well washed with ether until the ethereal extract no longer gave a precipitate with silver nitrate. After the ether and ethylamine had been carefully distilled off on the water bath, a product was obtained which distilled at 35—39° under a pressure of 10 mm. As it still contained some dichlorethylamine, it was treated with aluminium amalgam according to H. Wislicenus's method, and the fraction distilling at 35—37° was then found to be free from chlorine. This fraction, which consists of pure *ethyldiethylidenediamine*,  $NEt\langle{}^{CHMe}_{CHMe}\rangle NH$, is a colourless oil with an odour resembling that of camphor. It reduces warm ammoniacal silver nitrate and warm mercuric chloride solutions, but not Fehling's solution; water has no action on it, but acids hydrolyse the compound, yielding ammonia, aldehyde, ethylamine, and ethylhydroxylamine (or diethylhydroxylamine), if hydrochloric or oxalic acid is used. No alkylhydroxylamine is formed when sulphuric acid is used as the hydrolysing agent. J. J. S.

Amido-alcohols of the Fatty Series. By OSCAR PILOTY and OTTO RUFF (*Ber.*, 1897, 30, 2057—2068. Compare this vol., i, 453). —*Hydroxylamidodihydroxyisobutane* (2-methyl-2-hydroxylaminopropandiol-1:3), $CMe(NH\cdot OH)(CH_2\cdot OH)_2$, is obtained when Henry's tertiary nitroisobutylglycol (10 grams) is reduced with 2·5 per cent. sodium amalgam (285 grams) at 0° in the presence of crystallised aluminium sulphate (34·4 grams) and water (300 c.c.). The product is a syrup which solidifies within 1—2 days, and when crystallised from a mixture of alcohol and ether yields flat prisms melting at

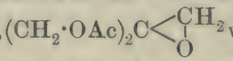
122—123° (corr.). It is readily soluble in water or alcohol, but only sparingly in ether or benzene; it reduces Fehling's solution in the cold, and has basic properties. The *picrate*, $C_4H_{11}NO_3,C_6H_2(NO_2)_3\cdot OH$, crystallises from a mixture of alcohol and light petroleum in yellow, prismatic needles melting at 134°; it is readily soluble in water or alcohol, moderately in ethylic acetate, and sparingly in ether or benzene. The *oxalate*, $(C_4H_{11}NO_3)_2,C_2H_2O_4$, crystallises from alcohol in thick, quadratic prisms melting at 95—96°, and decomposing at about 100°. It is readily soluble in water, and sparingly in ethylic acetate, but insoluble in ether or benzene.

Hydroxyacetoxime, $OH\cdot N\colon CMe\cdot CH_2\cdot OH$, is obtained when the hydroxylamine compound is oxidised with mercuric oxide. It was only obtained in the form of a syrup, but was identified by conversion into methylglyoxalosazone which Pechmann (Abstr., 1887, 1103) and Laubmann (Abstr., 1888, 366) have already prepared. Hydroxyacetoxime is obtained in a crystalline form when pure acetylcarbinol (hydroxyacetone) is treated with an alcoholic solution of hydroxylamine. It crystallises from chloroform in prisms melting at 71° (corr.), is readily soluble in water, alcohol or ether, moderately in hot chloroform, and sparingly in benzene.

The aliphatic amido-alcohols obtained by the reduction of the nitro-compounds or of the oximes are stable substances. Their salts are readily soluble in water and in some cases extremely hygroscopic; the sulphates and oxalates are sparingly soluble in absolute alcohol, and can therefore be made use of for isolating the bases.

Amidoglycerol (2-aminopropandiol-1 : 3), $CH(CH_2\cdot OH)_2\cdot NH_2$, which has only been obtained in aqueous solutions, possesses strong alkaline properties, and is capable of dissolving lead hydroxide and the oxides of copper and silver. It does not reduce Fehling's solution even on boiling. Its *hydrochloride* is formed together with ammonia and isopropylamine by the reduction of dihydroxyacetoxime (this vol., i, 453). The *sulphate*, which is so hygroscopic that it can be obtained in the crystalline form only from absolute alcohol, crystallises in compact plates. The *oxalate* crystallises from dilute alcohol in plates decomposing at 200°. *Trihydroxytertiarybutylamine* (2-methylol-2-aminopropandiol-1 :3), $C(CH_2\cdot OH)_3\cdot NH_2$, is obtained in the form of its *hydriodide* when tertiary nitroisobutylglycerol is reduced with hydriodic acid and yellow phosphorus. The salt crystallises from alcohol in strongly refractive crystals, $C_4H_{11}NO_3,HI + \frac{1}{2}C_2H_5\cdot OH$, melting at 105°; they rapidly effloresce on exposure to the air, and when dried melt at 188—189°. The free *base*, which is best obtained by treating the hydriodide with lead hydroxide, crystallises from its aqueous or alcoholic solution in long, compact needles melting at 167—168°; it is readily soluble in alcohol or water, sparingly in acetone, and practically insoluble in ether. It dissolves the hydroxides of lead, silver or copper, but not aluminium hydroxide, and it does not reduce Fehling's solution. The *hydrochloride* obtained when nitroisobutylglycerol is reduced with tin and hydrochloric acid, crystallises from alcohol in strongly refractive, six-sided plates, melting at about 149°, and decomposing at about 230°. The *sulphate* crystallises in thin, six-cornered plates melting at 167°. The *oxalate* crystallises in needles which decompose at 188°. The compounds with gold chloride, potassium, bismuthoiodide and also with picric acid are extremely readily soluble in alcohol. Sodium nitrite reacts with an aqueous solution of the hydrochloride yielding the nitrite of the base, and when this is warmed, gas is evolved and an oily substance, probably the alcohol, can be extracted from the residue. A *triacetyl* derivative of the hydrochloride, namely,

$$C(CH_2{\cdot}OAc)_3{\cdot}NH_2,HCl,$$

is obtained together with the *tetracetyl* derivative, $C(CH_2{\cdot}OAc)_3{\cdot}NHAc$, when the hydrochloride (5 grams) is heated on the water bath for 6 hours with acetic anhydride (15 grams) and glacial acetic acid (20 grams). The triacetyl derivative crystallises in thin, elastic needles, or in compact, rhombic prisms melting at 132—133°. It is readily soluble in water, alcohol, ethylic acetate, or acetone, sparingly in benzene and almost insoluble in ether, or light petroleum. When treated with sodium nitrite, an oil which is sparingly soluble in water, and which the authors regard as impure *triacetoxyisobutane* is formed. This oil, when distilled under diminished pressure, is converted into acetic acid and a *diacetyl* derivative of an *inner anhydride of isobutylglycerol* (trihydroxyisobutane),  $(CH_2{\cdot}OAc)_2C{<}\begin{matrix}CH_2\\ | \\ O\end{matrix}$ which distils at 174—176° under a pressure of 20 mm. This compound, tetracetylmethylolaminopropandiol, $C(CH_2{\cdot}OAc)_3{\cdot}NHAc$, is readily soluble in ether, alcohol, and benzene, and may be salted out from its aqueous solutions. It does not combine with hydrogen chloride, and crystallises from water in broad prisms melting at 114—115°.

Tertiary isobutylglycolamine (2-methyl-2-aminopropandiol-1 : 3), $CMe(CH_2{\cdot}OH)_2{\cdot}NH_2$, is obtained in the form of its hydrochloride by the reduction of nitroisobutylglycol with tin and hydrochloric acid. The *hydrochloride*, $C_4H_{11}NO_2.HCl$, which crystallises from a mixture of alcohol and ether in prismatic needles melting at 91—92°, is extremely hygroscopic, and dissolves readily in alcohol, but is insoluble in ether. The *sulphate* crystallises in pointed needles decomposing at about 225°, it is extremely hygroscopic, but is practically insoluble in cold alcohol. The *oxalate* crystallises from alcohol in flat, rhombic needles which decompose at about 215°. It dissolves readily in water, but is not hygroscopic. The free base is obtained in the form of a syrup by the action of lead hydroxide or silver oxide on the base, it cannot be completely dried over sulphuric acid, and when distilled under a pressure of 16·5 mm. the greater part is decomposed but yields a small quantity of crystals melting at 60—95°. The strongly alkaline solution dissolves cupric hydroxide, silver oxide, and to a certain extent silver chloride, but it does not reduce Fehling's solution.

J. J. S.

The Double Aldehyde of Suberic Acid. By ADOLF VON BAEYER (*Ber.*, 1897, **30**, 1962—1965).—The ease with which α-hydroxypinic acid is converted by lead peroxide into the aldehyde-acid containing 1 carbon atom less than itself, seemed to show that this reaction might be generally applicable, and it was found that dihydroxysebacic acid, prepared from the dibromo-acid by treatment with silver oxide, gave the *dialdehyde of suberic acid*, $CHO{\cdot}[CH_2]_6{\cdot}CHO$, when treated with lead peroxide; during the process of oxidation, however, it was necessary to have a strong acid present, in order to prevent the formation of a lead salt of the acid, and for this purpose phosphoric acid was found to be the most serviceable. The dialdehyde distils, with partial decomposition, at 230—240°, but if kept, quickly polymerises to a hard, vitreous mass. Its aqueous solution smells like oenanthaldehyde and shows all the reactions of an aldehyde, forming a *hydroxylamine* compound which crystallises from alcohol in prisms melting at 150—155°, also a *semicarbazone* melting at 183—185°. On oxidation with permanganate, it is converted into suberic acid. J. F. T.

Methyl Derivatives of Acetylmethyl Hexyl Ketone (2 : 4-Decadione). By J. KRAMERS (*Rec. Trav. Chim.*, 1897, **16**, 116—125).—Claisen and Ehrhardt (*Ber.*, **22**, 1016) have demonstrated that, when an acetyl group is introduced into methyl propyl ketone, it enters the methyl and not the propyl group, and proved this by showing that the condensation product of ethylic butyrate and acetone is acetylmethyl propyl ketone (2 : 4-heptadione), and is identical with the product of the action of ethylic acetate on methyl propyl ketone. The author has proved this by another means, using methyl hexyl ketone.

If it be admitted that the condensation of methyl hexyl ketone with ethylic acetate can only take place in one of the following ways,

$$\text{(I)}\ CH_3\cdot COOEt + CH_3\cdot CO\cdot C_6H_{13} = CH_3\cdot CO\cdot CH_2\cdot CO\cdot C_6H_{13} + Et\cdot OH$$
$$\text{(II)}\ CH_3\cdot COOEt + CH_3\cdot CO\cdot CH_2\cdot C_5H_{11} = CH_3\cdot CO\cdot CH(C_5H_{11})\cdot CO\cdot CH_3 + Et\cdot OH,$$

it is evident that the product from I has 2 atoms of hydrogen capable of being replaced by alkyl groups, whilst that of II has only one.

The author has succeeded in preparing both the mono- and dimethyl-derivatives of acetylmethyl hexyl ketone, and finds, in contradistinction to what Claisen says, that the monomethyl derivative gives, at once, a compound with copper acetate of a dirty green colour, whilst the copper derivative of the nonmethylated diketone is violet-blue, and the dimethylated diketone gives no copper derivative at all.

A common property of all compounds containing the grouping R·CO·CHR·COR, except malonic acid and its derivatives, is the production of a dark red coloration with an alcoholic solution of ferric chloride; the above-mentioned diketone and its monomethyl derivative give this characteristic reaction, whilst with the dimethylated diketone only a feeble yellowish colour is obtained.

The author has tried the action of potash on the monomethyl derivative, but the amount of material at his disposal was insufficient to satisfactorily prove where fission takes place with this ketone.

Acetylmethyl hexyl ketone, prepared by the action of ethylic acetate on methyl hexyl ketone, is a colourless liquid boiling at 130—131° under a pressure of 23 mm., and solidifying at −6°. It has a specific gravity of 0·913 at 15°, and the molecular weight, as determined by Beckmann's method, is 157, instead of 170 as required by the formula $C_{10}H_{18}O_2$.

Monomethyl acetylmethyl hexyl ketone (3-methyldecadione-2 : 4 or α-acetylethyl hexyl ketone, $COMe \cdot CHMe \cdot CO \cdot C_6H_{13}$), is obtained by the action of methylic iodide on the diketone. It is a colourless liquid with a peculiar odour, boiling at 143—144° under a pressure of 23 mm.; it does not solidify at a temperature of $-40°$. It has a specific gravity $= 0{\cdot}916$ at 15°, and a molecular weight of 170 (calculated 184).

Dimethyl acetylmethyl hexyl ketone (dimethyl-3-decadione-2 : 4, α-acetylisopropyl hexyl ketone), $COMe \cdot CMe_2 \cdot CO \cdot C_6H_{13}$, prepared by the action of methylic iodide on the monomethyl derivative, is a colourless, peculiar-smelling liquid boiling at 142·5—143·5° at a pressure of 18 mm., and does not solidify at $-40°$. Its specific gravity $= 0{\cdot}912$ at 15°, and the molecular weight is 180 (calculated 198). A. W. C.

δε-Heptenoic Acid. By FRITZ FICHTER and EUGEN GULLY (*Ber.*, 1897, **30**, 2047—2050).—δε-Unsaturated acids can be obtained by a method similar to that previously used for the preparation of γδ-unsaturated acids (this vol., i, 13). *Ethylic acetyladipate*, $COOEt \cdot CHAc \cdot [CH_2]_3 \cdot COOEt$, obtained by the action of ethylic γ-chlorobutyrate on ethylic sodioacetoacetate, distils at 160° under a pressure of 12 mm. The ethylic salt, when subjected to ketonic hydrolysis, yields Perkin's ω-acetylvaleric acid (Trans., 1890, 229) whilst acid hydrolysis gives rise to adipic and acetic acids. When ethylic acetyladipate is reduced with aqueous alcohol and sodium amalgam (4 per cent.) and the solution kept neutralised as far as possible with hydrochloric acid, the chief products are adipic acid and *ε-hydroxy-α-ethyladipic acid*, $COOH \cdot CH(CHMe \cdot OH) \cdot [CH_2]_3 \cdot COOH$; these can be separated by means of chloroform in which adipic acid is insoluble. The new acid was obtained as a syrup; but its *barium*, *calcium*, and *silver* salts were prepared and analysed. When distilled, the acid decomposed into carbonic anhydride, water, ethylideneadipic acid, and δε-heptenoic acid. *Ethylideneadipic acid*, $CHMe\dot{:}C(COOH) \cdot [CH_2]_3 \cdot COOH$, crystallises from water, melts at 130°, and is not volatile with steam. *δε-Heptenoic acid*, $CHMe\dot{:}CH \cdot [CH_2]_3 \cdot COOH$, is readily volatile with steam, and is isomeric with Schmidt's acid (*Annalen*, **255**, 77). The *calcium* salt crystallises with $1H_2O$, but the *cadmium* and *silver* salts are anhydrous. The acid combines with bromine, yielding an oily *dibromide*, and with hydrogen bromide, yielding an oily *hydrobromide*, which, when boiled with water, is converted into *δ-hydroxyheptoic acid*. The *barium* salt of the hydroxy-acid is readily soluble in water, and melts at 80—90°; the *silver* salt is obtained as a colourless precipitate. The free hydroxy-acid, when boiled with hydrochloric acid, is partially converted into a *δ-lactone*, which, however, readily passes back again into the acid. J. J. S.

α-Hydroxy-α-methyladipic Acid and δε-Hexenoic Acid. By FRITZ FICHTER and WERNER LANGGUTH (*Ber.*, 1897, **30**, 2050—2053). —*α-Hydroxy-α-methyladipic acid*, $COOH \cdot CMe(OH) \cdot [CH_2]_3 \cdot COOH$, is obtained by the hydrolysis of the nitrile formed by the action of potassium cyanide and hydrochloric acid on Woulff's acetobutyric acid (*Annalen*, **216**, 130). It crystallises from a mixture of ether and light petroleum in small needles melting at 92°. The *silver* salt is an amorphous precipitate, and the *alkaline earth* salts are readily soluble in water. When heated for some time at 100° the acid yields the corresponding lactonic acid, *hexo-δ-lactone-δ-carboxylic* acid, which is extremely hygroscopic and unstable.

When distilled in small portions, α-hydroxy-α-methyladipic acid yields a small quantity of the lactone, together with a non-volatile dibasic unsaturated *acid*, $C_7H_{10}O_5$, melting at 153°, and about equal quantities of γδ- and δε-hexenoic acids, both of which are volatile with steam. These two acids are most conveniently separated by means of their barium salts, the barium salt of the γδ-acid being practically insoluble in alcohol (this vol., i, 13), whereas the isomeric salt is readily soluble. *δε-Hexenoic acid* boils at 202—204°, and does not solidify in a freezing mixture. The *barium* salt is anhydrous, and is readily soluble in alcohol or water; the *calcium* salt is also readily soluble, and crystallises with $1H_2O$. The *cadmium* and *silver* salts are amorphous. The acid readily combines with hydrogen bromide, and when the compound thus formed is boiled with water, Woulff's capro-δ-lactone (hexo-δ-lactone) is obtained (*Annalen*, **216**, 135). J. J. S.

Castor Oil. By HANS MEYER (*Arch. Pharm.*, 1897, **235**, 184—191).—In reference to Juillard's observation (Abstr., 1895, i, 500) that dihydroxystearic acid is contained in castor oil, the author states that he had also isolated this compound at the time of his previous research (*Arch. expt. Path. Pharm.*, 1890, **28**, 145) by the action of dilute hydrochloric acid on the purified calcium salt prepared by Claus's method. The ethereal solution, after washing and standing, deposits crystalline leaflets which melt at 140—141°, and closely resemble cholesterol. They are, however, insoluble in ether, and do not form an additive compound with bromine. Analysis indicates an empirical formula, $C_{18}H_{36}O_4$. From 2 kilograms of oil, 1·5 grams of pure substance are obtained. Attempts to prepare this compound by heating ricinoleic acid with water at 300°, or with sodium hydroxide solution at 200°, failed.

Juillard found that the triglyceride of ricinoleic acid could not be prepared by Berthelot's method owing to the polymerisation of the acid, whereby a glyceride of polyricinoleic acid was produced. The author finds that preparations of the pure acid which originally had a sp. gr. = 0·9460 at 12°, after a lapse of eight years had become more viscous, of a sp. gr. = 0·9680 at 12°, and required about one-third less alcoholic potassium hydroxide solution for neutralisation. Hübl's iodine number was also found to have diminished from 85·53 for the freshly prepared acid to 64·06. The specific gravity, saponification number, and molecular refraction agree with the numbers calculated on the assumption that these old preparations are a mixture of 30 parts of ricinoleic acid with 70 parts of diricinoleic acid. By the action of alcoholic potash, ordinary ricinoleic acid may be obtained.

The author has succeeded in preparing the triglyceride of ricinoleic acid by passing a slow stream of carbonic anhydride into a mixture of the acid with glycerol, and heating at 280—300°. The product, freed from excess of glycerol by the addition of water, forms an almost colourless neutral oil possessing the same viscosity, taste, and physiological action as castor oil. It dissolves in 96 per cent. alcohol and in methylic alcohol, whereas Juillard's glycerides of polyricinoleic acid only partially dissolve. The saponification number agrees with that of the triglyceride. The sp. gr. of two preparations was 0·959 and 0·984 respectively, whilst that of ordinary castor oil is 0·95 to 0·97, and that of the oil freed from stearates by cooling to +5° is 0·9635 at 15°. Specific rotatory power $[\alpha]_D = +5{\cdot}16°$; for castor oil $[\alpha]_D = +4{\cdot}68°$. Hübl's iodine number = 71—86·4, the calculated number for the pure triglyceride being 81·62, whilst that of ordinary castor oil is 84·0—84·7. The synthetically prepared oil, unlike the ordinary oil, does not form solid ricinelaidine by the action of nitrous acid, but only becomes more viscous.

The sp. gr. of triglyceride preparations which had been kept eight years was found also to have increased, in one case to 0·9980 at 14·5°, in another to 1·009. The numbers calculated from Traube's constants for the simple formula $C_{57}H_{104}O_9$, are 0·995 for the double formula, and 1·000 for the treble, hence polymerisation has evidently taken place. This must have been effected by simple physical association of the molecules, or more probably by union with disappearance of the double bonds, for condensation between carboxyl and hydroxyl groups as in the case of the free acid, is here impossible. The iodine number was also found to have become less. The author regards Juillard's preparation, which is stated to be a mixture of two molecular proportions of triricinolein with one of diricinolein, as the nearly pure diglyceride of ricinoleic acid, with which assumption Juillard's saponification number very nearly agrees; he thinks that the determination of the molecular weight by Raoult's method may have been vitiated by polymerisation of the glyceride. E. W. W.

Hydroxymethylene Compounds. By LUDWIG CLAISEN (*Annalen*, 1897, **297**, 1—98. Compare Abstr., 1894, i, 66, and 1895, i, 62).—*Methylic ethoxymethyleneacetoacetate*, OEt·CH:CAc·COOMe, is prepared by heating methylic acetoacetate with ethylic orthoformate and acetic anhydride in a reflux apparatus (compare *loc. cit.*); it boils at 173—174° under a pressure of 45 mm., and slightly decomposes when it is distilled under the ordinary pressure at 265—268°.

Ethylic methoxymethyleneacetoacetate, OMe·CH:CAc·COOEt, is prepared from the silver derivative of ethylic hydroxymethyleneacetoacetate and methylic iodide; it boils at 150—152° under a pressure of 19 mm; the *methylic* salt, obtained from methylic acetoacetate, methylic orthoformate, and acetic anhydride, boils at 150° under a pressure of 16 mm.

Although ethylic hydroxymethyleneacetoacetate is produced when the ethoxy-compound is treated with water, it is more conveniently prepared by agitating the substance with a concentrated, aqueous solution of copper acetate, which gives rise to the *copper* derivative of ethylic hydroxymethyleneacetoacetate; the *potassium*, *barium*, *calcium*, *magnesium*, and *silver* derivatives are anhydrous, and the *ammonium* derivative melts at 104—105°.

Methylic hydroxymethyleneacetoacetate, OH·CH:CAc·COOMe, prepared by the action of aqueous copper acetate on the corresponding ethoxy-compound, has a sp. gr. = 1·186 at 15°, and boils at 110° and 185° under pressures of 57 mm. and 750 mm. respectively. The *copper* derivative crystallises from methylic alcohol in lustrous leaflets, and melts at 207—208°.

When ethylic hydroxymethyleneacetoacetate is hydrolysed with the calculated quantity of a boiling, normal solution of caustic soda, ethylic acetoacetate and sodium formate are produced; boiling water alone gives rise to triacetylbenzene, hydroxymethyleneacetone being formed as an intermediate compound. Oxidation of ethylic hydroxymethyleneacetoacetate with silver nitrate resolves it into ethylic acetoacetate and carbonic anhydride.

Ethylic amidomethyleneacetoacetate, $\mathrm{NH_2{\cdot}CH{:}CAc{\cdot}COOEt}$, prepared by the action of alcoholic ammonia on ethylic ethoxymethyleneacetoacetate, crystallises in beautiful, colourless plates, melts at 55°, and boils at 176—179° under a pressure of 15 mm. The compound behaves like an amide, and forms a *potassium* derivative, which yields ammonia when heated in aqueous solution; the *copper* derivative crystallises from alcohol in bluish-violet scales, and melts and effervesces at 195—198°. The *benzoyl* derivative is prepared by the action of benzoic chloride on the base, and also by heating ethylic ethoxymethyleneacetoacetate with benzamide at 150°; it crystallises from alcohol in pale yellow needles and prisms, and melts at 95°. The *acetyl* derivative forms long, colourless needles, and melts at 88°. The *carbamide* derivative, $\mathrm{NH_2{\cdot}CO{\cdot}NH{\cdot}CH{:}CAc{\cdot}COOEt}$, obtained by heating ethylic ethoxymethyleneacetoacetate with carbamide at 140°, crystallises from alcohol in white leaflets, melting at 191—192°; the *anilide*,

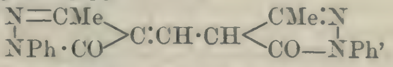
$$\mathrm{NHPh{\cdot}CH{:}CAc{\cdot}COOEt},$$

forms bright yellow, lustrous plates, and melts at 45—46°.

Methylic amidomethyleneacetoacetate crystallises from benzene in needles, and melts at 109°. The *anilide* and *paratoluidide* melt at 84—85°, and 86—87°, respectively.

Ethylic methenylbisacetoacetate, $\mathrm{COOEt{\cdot}CAc{:}CH{\cdot}CHAc{\cdot}COOEt}$, is prepared by heating ethylic acetoacetate (2 mols.), ethylic orthoformate (1 mol.), and acetic anhydride (3 mols.), in a reflux apparatus for half a day (*loc. cit.*), or more conveniently, by the action of ethylic ethoxymethyleneacetoacetate on alcoholic ethylic sodioacetoacetate at the ordinary temperature. It crystallises from petroleum or carbon bisulphide in aggregates of short prisms, and melts at 96°; ferric chloride develops a bluish-violet coloration with the alcoholic solution.

Methenylbisphenylmethylpyrazolone,



$$\begin{array}{l}\mathrm{N{=}CMe}\\ \mathrm{NPh{\cdot}CO}\end{array}\!\!>\mathrm{C{:}CH{\cdot}CH}<\!\!\begin{array}{l}\mathrm{CMe{:}N}\\ \mathrm{CO{-}NPh}\end{array},$$

obtained from phenylmethylpyrazolone and ethylic orthoformate, crystallises from ethylic acetate in orange-yellow needles, and melts at 180—181°. It is probably identical with the compound obtained by Besthorn and Knorr from the sodium derivative of phenylmethylpyrazolone and chloroform.

Ethylic methenylbisacetoacetate yields ethylic 2 : 6-dimethylpyridine-3 : 5-dicarboxylate when heated with ammonium acetate and glacial acetic acid in a reflux apparatus. Alcoholic sodium ethoxide converts the salt into *monethylic metahydroxyuvitate*,

$$\mathrm{COOEt{\cdot}C_6H_2Me(OH){\cdot}COOH};$$

the *sodium* salt contains $3H_2O$, and melts and decomposes at 230—231°, the *silver* salt is anhydrous, and the *barium* salt contains $4H_2O$. The identity of the acid is established by hydrolysis, which converts it into metahydroxyuvitic acid, and by conversion into the *diethylic* salt of metahydroxyuvitic acid, which crystallises from petroleum in colourless plates melting at 50—51°; moreover, elimination of carbonic anhydride under the influence of heat converts the monethylic salt into *ethylic homoparahydroxybenzoate* [$OH : Me : COOEt = 2 : 6 : 5$], which melts at 92—93°, and boils at 306—308°.

Xanthophanic acid, $C_{18}H_{20}O_8$, is obtained by heating finely-powdered ethylic sodioacetoacetate (15·2 grams) with ethylic ethoxymethyleneacetoacetate (37·2 grams) in a reflux apparatus; it crystallises from alcohol in hemispherical aggregates of brownish-yellow needles, and melts at 143—144°. This compound is almost insoluble in water, but dissolves somewhat readily in cold benzene and glacial acetic acid, and very readily in chloroform; the alcoholic solution stains the skin intensely red, and develops a dark brownish-red coloration with ferric chloride. The solution in oil of vitriol is dark red, and exhibits beautiful fluorescence when heated. Ammonia, alkali carbonates, and a hot solution of potassium acetate dissolve the acid with production of a dark red coloration, and the solutions may be boiled without undergoing change, provided no caustic alkali is present. Xanthophanic acid is also formed when ethylic ethoxymethyleneacetoacetate is heated with potassium acetate and alcohol on the water bath. The *potassium*, *sodium*, and *barium* salts are red, crystalline substances, and dissolve readily in water. When boiled with excess of caustic soda, the sodium salt yields a colourless *compound*, $C_{15}H_{16}O_7$, which crystallises in short prisms, and melts at 118—120°; it is insoluble in water, but forms a golden-yellow solution in sodium carbonate, and the alcoholic solution develops a dark reddish-violet coloration with ferric chloride.

Glaucophanic acid, $C_{27}H_{26}O_{12}$, is a bye-product in the preparation of xanthophanic acid, forming about 10 per cent. of the product of the action of ethylic sodioacetoacetate on ethylic ethoxymethyleneacetoacetate; it crystallises from benzene in small, black needles with brownish-green reflex, and melts at 188—189°. It is scarcely soluble in cold water, but dissolves sparingly when the water is boiling, forming a dark blue solution; oil of vitriol also produces a dark blue solution. The *sodium* salt is very sparingly soluble in alcohol, from which it crystallises in small, green needles, with bronze reflex; the *ammonium* salt forms lustrous, greenish crystals.

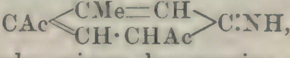
Methoxymethyleneacetylacetone, $OMe{\cdot}CH{:}CAc_2$, is prepared by heating acetylacetone, acetic anhydride, and methylic orthoformate in a reflux apparatus for 40 minutes; it is a colourless oil which becomes red when kept, melts at 6—7°, and boils at 140° under a pressure of 16 mm.

When hydroxymethyleneacetylacetone (Abstr., 1894, i, 66), obtained by the action of water on ethoxymethyleneacetylacetone, is exposed to air, it gradually softens and becomes converted into an oil of penetrating and disagreeable odour, which liberates carbonic anhydride when heated; the alcoholic solution of hydroxymethyleneacetylacetone develops a dark, yellowish-red coloration with ferric chloride, and the solution in oil of vitriol is pale yellow. Hydroxymethyleneacetylacetone is strongly acidic, and the solution in aqueous alcohol turns blue litmus red; the molecular conductivity in an infinitely dilute solution $\mu_\infty = 195$ at 2·6°. Hot caustic soda resolves it into formic aid and acetylacetone, and hot water alone produces the same effect after some time, a small portion of the substance becoming converted into triacetylbenzene. It is oxidised by mercuric oxide, yielding carbonic anhydride and acetylacetone. The *calcium* derivative contains $2H_2O$, but the *barium* and *silver* derivatives are anhydrous; the *mercurous* derivative is a yellowish-white, crystalline substance, becoming black spontaneously and depositing mercury; the *copper* derivative melts at 214°, the *ferric* derivative forms scarlet crystals melting at 124°, and the *ferrous* derivative brownish-yellow crystals. The *benzoyl* derivative of hydroxymethyleneacetylacetone crystallises from alcohol and melts at 71°; it becomes brown and soft when exposed to the air.

Amidomethyleneacetylacetone, $NH_2{\cdot}CH{:}CAc_2$, prepared by the action of alcoholic ammonia on ethoxymethyleneacetylacetone, crystallises from water in large, lustrous needles, melting at 144°; it gives no coloration with ferric chloride, but forms a crystalline, bluish-violet *copper* derivative, which dissolves in organic solvents and melts at 218°. The *acetyl* derivative crystallises from ethylic acetate in needles melting at 62°, and the *benzoyl* derivative also forms needles which melt at 101°; the *carbamide* derivative crystallises from alcohol in white needles and prisms, and melts and evolves gas at 187°. The *anilide* of hydroxymethyleneacetylacetone, $NHPh{\cdot}CH{:}CAc_2$, crystallises from petroleum in long, colourless needles, and melts at 90—91°; the *paratoluidide* and *benzylanilide* melt at 139—140° and 106° respectively.

Methenylbisacetylacetone, $CAc_2{:}CH{\cdot}CHAc_2$, is prepared by heating ethoxymethyleneacetylacetone, dissolved in absolute alcohol, with the potassium derivative of acetylacetone; it crystallises from ethylic acetate in aggregates of short, colourless prisms, and melts at 117—118° to a dark red liquid (Abstr., 1894, i, 67). The alcoholic solution develops a dark red coloration with ferric chloride, and the aqueous solution has an intensely bitter taste; the solutions in dilute alkalis, and alkali carbonates are golden yellow.

When an aqueous solution of the potassium derivative of methenylbisacetylacetone is boiled in a reflux apparatus for 6—8 hours, it yields *diacetylmetacresol* $[OH : Ac_2 = 3 : 4 : 6]$ which crystallises from dilute acetic acid in long, white, lustrous needles, melts at 112°, and boils at 310°; the alcoholic solution develops a reddish-violet coloration with ferric chloride, and is sufficiently acidic to redden blue litmus paper. Dilute aqueous alkalis dissolve the substance readily, and it is also soluble in alkali carbonates, forming colourless solutions; the *potassium* and *barium* derivatives are colourless, crystalline substances. Ammonia converts diacetylmetacresol into the *compound*



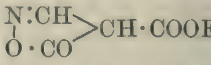
$CAc{<}\begin{matrix}CMe{=}CH\\CH{\cdot}CHAc\end{matrix}{>}C{:}NH$

which crystallises from alcohol in long, slender prisms, decomposing and melting indefinitely at 235°, after softening and becoming brown at 226°; when carefully heated, it sublimes in a woolly mass of needles. The substance is isomeric with 3 : 5-diacetyl-2 : 6-dimethylpyridine (m. p. 73—74°), which is produced by the action of aqueous ammonia on methenylbisacetylacetone; the solution in cold dilute sulphuric acid is colourless, and precipitates the unchanged substance when treated with ammonia, but if the liquid is heated previously to the treatment with alkali, diacetylmetacresol is regenerated.

With E. Hasse.—Ethylic ethoxymethylenemalonate (*loc. cit.*) is prepared by heating ethylic malonate and ethylic orthoformate with acetic anhydride and zinc chloride in a reflux apparatus. Aqueous ammonia converts it into *ethylic amidomethylenemalonate*, $NH_2\cdot CH\colon C(COOEt)_2$, which crystallises from petroleum in colourless plates and short prisms, melting at 67°; it is therefore identical with ethylic amidoethylenedicarboxylate (Ruhemann and Morrell, Abstr., 1895, i, 20), *ethylic anilidomethylenemalonate* being identical with *ethylic anilidoethylenedicarboxylate* (*loc. cit.*).

Methylic methoxymethylenemalonate, $OMe\cdot CH\colon C(COOMe)_2$, crystallises from a mixture of ethylic acetate and petroleum in aggregates of needles; it melts at 46°, and boils at 167° under a pressure of 20 mm.

Ethylic hydroxymethylenemalonate, $OH\cdot CH\colon C(COOEt)_2$, is obtained by treating an ethereal solution of the ethoxy-compound with the calculated quantity of alcoholic potash; it is a colourless oil, which boils at 107—109° under a pressure of 12 mm., and at 217—219° at the ordinary pressure; it has a sp. gr. = 1·128 at 20°. The alcoholic solution reddens blue litmus, and develops a dark, orange-red coloration with ferric chloride. The *potassium* derivative crystallises in short prisms, the *barium* derivative in white plates, and the *silver* derivative is crystalline, rapidly yielding the metal; the *copper* derivative crystallises from dilute alcohol in pale green needles melting at 119° when hydrated, and becomes dark green after removal of $1H_2O$, melting at 138° in the anhydrous condition.

Ethylic isoxazolone-β carboxylate,  $\begin{array}{l} N\colon CH \\ | \\ O\cdot CO \end{array}\!\!>CH\cdot COOEt$, is prepared by heating ethylic ethoxymethylenemalonate with an alcoholic solution of hydroxylamine during 2 hours on the water bath; it separates from alcohol in small, white needles, and when crystallised from water resembles benzoic acid. When heated slowly, it melts, decomposing completely at 160—165°, this change taking place at 183—185° when the temperature rises quickly; the *silver* derivative is white and crystalline, the *ethyl* derivative crystallises in white needles, and melts at 46°, and the *methyl* derivative forms white needles and prisms melting at 96—97°. The action of hydroxylamine on ethylic ethoxymethylenemalonate is comparable with the behaviour of this substance towards phenylhydrazine, which gives rise to ethylic 1 : 5 : 4-phenylpyrazolonecarboxylate (Abstr., 1895, i, 193).

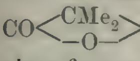
Ethylic methenylbismalonate (*ethylic dicarboxyglutaconate*),

$$(COOEt)_2C\colon CH\cdot CH(COOEt)_2,$$

is obtained by treating an alcoholic solution of ethylic sodiomalonate with the calculated quantity of ethylic ethoxymethylenemalonate; it is the intermediate production of this substance which accounts for the residue of ethylic ethoxycoumalindicarboxylate obtained on distilling ethylic ethoxymethylenemalonate. Ruhemann and Guthzeit, who first prepared ethylic dicarboxyglutaconate, considered it remarkable that alkaline agents should so easily resolve the substance into malonic and formic acids. In the author's opinion, this change is explained by the fact that condensation products of organic acids with aliphatic compounds are, in general, easily resolved into their components by alkalis; moreover, those substances which contain negative radicles attached to ethylenic carbon frequently undergo decomposition involving assimilation of water, followed by rupture of the carbon chain, as instanced by the resolution of mesitylic oxide into two molecular proportions of acetone.

A valuable summary of facts relating to the production of hydroxymethylene compounds forms the conclusion of the paper.

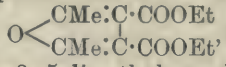
M. O. F.

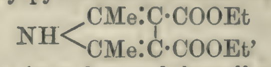
β-Lactone of *as*-Dimethylmalic Acid. By Adolf von Baeyer and Victor Villiger (*Ber.*, 1897, **30**, 1954—1958).—The existence of β-lactones of saturated open carbon chains has long been a matter of speculation, it is now found, however, that if the *monobrom*-as-*dimethylsuccinic acid* which crystallises from hydrochloric acid and melts at 167° be treated with silver oxide, the β-lactone of dimethylmalic acid,  $\mathrm{CO}{<}\begin{matrix}\mathrm{CMe_2}\\ \mathrm{-O-}\end{matrix}{>}\mathrm{CH\cdot COOH}$, is produced. When first formed, the lactone gives figures on analysis corresponding with dimethylmalic acid, but on drying in a vacuum it gradually loses $1H_2O$, and then agrees with the lactone formula. The dried substance melts at 45—47°, but readily takes up $1H_2O$, melting then at 54—55°; titration of the dried substance showed it to be monobasic in the cold, but dibasic when warm, and a molecular weight determination proved it to be in reality a lactone, and not a lactide.

The lactone does not give off carbonic anhydride on distillation, and is obtained unchanged on evaporating its aqueous solution on the water bath; in the presence of alkali, however, it is instantly converted into dimethylmalic acid melting at 129—131°. The lactone is not re-formed from the acid when the latter is heated. J. F. T.

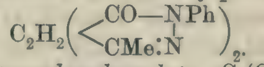
***cis*- and *trans*- Isomerism of Lactones.** By Adolf von Baeyer and Victor Villiger (*Ber.*, 1897, **30**, 1958—1962).—The isomerism between the two lactonic acids of hydroxycamphoronic acid, which are obtained by the bromination of camphoronic acid, must be geometric, since camphoronic acid, according to Bredt's formula, can only yield one hydroxy-derivative; the lactonic acid of hydroxydimethyltricarballylic acid was therefore prepared, and it was found that this compound existed in both the *cis* and the *trans* forms, the free carboxyl group in the former being on the one side of the lactone ring. and in the latter on the other side. The cis-*lactonic acid of hydroxydimethyltricarballylic acid*, prepared by decomposing bromodimethyltricarballylic acid with water, crystallises from water in large, many-sided prisms, melting at 207°. The trans-*lactonic acid* is the chief product formed in the oxidation, by means of chromic acid, of the dioxyisocamphoronic acid obtained from brominated isocamphoronic acid by treatment with baryta; it is somewhat less soluble in water than the *cis*-modification, and forms slender prisms melting at 211—212°; on heating the *cis*-lactonic acid for 15 hours at 150°, it is for the most part (90 per cent.) converted into the *trans*-modification, and on heating the *trans*-acid in a similar way, a small quantity of the *cis*-compound is always produced. J. F. T.

Some Derivatives of Ethylic Diacetylsuccinate and Dibenzoylsuccinate. By CARL PAAL and FRIEDR. HÄRTEL (*Ber.*, 1897, **30**, 1991—1998).—Ethylic diacetylfumarate (Just, Abstr., 1886, 141) forms, with phenylhydrazine, a compound, $C_{22}H_{22}N_4O_3$; this melts at 138°, and decomposes when heated further, but yields no pyrazole-blue. *Ethylic dibenzoylfumarate*, $C_2Bz_2(COOEt)_2$, is obtained by suspending the sodium derivative of ethylic dibenzoylsuccinate in ether and acting on it with iodine; it melts at 75°. Boiled in acetic acid solution with occasional addition of strong ammonia, it yields ethylic 2 : 5-diphenylpyrroline-3 : 4-dicarboxylate, melting at 150—151° (Knorr, this vol., i, 66); if it is heated in acetic acid solution, and aqueous ammonia is then added, a substance melting at 195° is obtained. When hydrolysed with alcoholic alkali, it yields, beside an oil, two crystalline acids, one of which melts at 157—158°, and is presumably *dibenzoylmalic acid*, $COOH\cdot CHBz\cdot CBz(OH)\cdot COOH$.

Ethylic bis-benzoyloxycrotonate, $C_2(CMe\cdot OBz)_2(COOEt)_2$, is obtained by suspending ethylic sodiodiacetylsuccinate in ether and treating it with benzoic chloride; it melts at 101°, and is converted by concentrated sulphuric acid into benzoic anhydride and ethylic carbopyrotritarate,  $\mathrm{O}<\begin{matrix}\mathrm{CMe{:}C\cdot COOEt}\\ \mathrm{CMe{:}C\cdot COOEt}\end{matrix}$, by alcoholic ammonia into benzamide and ethylic 2 : 5-dimethylpyrroline-3 : 4-dicarboxylate,

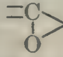


$$\mathrm{NH}<\begin{matrix}\mathrm{CMe{:}C\cdot COOEt}\\ \mathrm{CMe{:}C\cdot COOEt}\end{matrix}$$

and by phenylhydrazine into benzoylphenylhydrazine and bisphenylmethylpyrazolone  $\mathrm{C_2H_2}\left(<\begin{matrix}\mathrm{CO{-}NPh}\\ \mathrm{CMe{:}N}\end{matrix}\right)_2$.

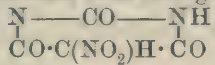
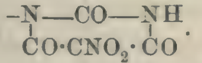
Ethylic bis-acetoxyphenylacrylate, $C_2(CPh\cdot OAc)_2(COOEt)_2$, is obtained by suspending ethylic sodiodibenzoylsuccinate in ether and treating it with acetic anhydride; it melts at 106°. By using benzoic instead of acetic chloride, *ethylic bis-benzoyloxyphenylacrylate*, $C_2(CPh\cdot OBz)_2(COOEt)_2$ can be obtained; it melts at 204°. C. F. B.

Xanthine Bases from Uric Acid. By ERNST EDUARD SUNDVIK (*Zeit. physiol. Chem.*, 1897, **23**, 476—482).—Although the relationship between uric acid and xanthine bases is undoubted, the observation of Strecker's, that uric acid can be converted into hypoxanthine by the use of sodium amalgam, is not confirmed. By heating an alkaline solution of uric acid, however, with chloroform, there were found, in addition to humous products, a substance, the silver compound of which contains from 83—84 per cent. of silver; silver cyanamide contains 84. In later experiments, two other substances were obtained, one of which resembles xanthine, the other hypoxanthine, but the identity is not absolute. W. D. H.

Nitrobarbituric and Nitrodimethylbarbituric Acids. By Arnold F. Holleman (*Rec. Trav. Chim*, 1897, **16**, 162—171).—Nitrobarbituric and nitrodimethylbarbituric acids are nitroaliphatic compounds in which the *iso*-form is the stable one. The author has shown that several isonitro-compounds have an intense yellow colour in aqueous solutions; this appears to be always the case where the grouping  $\overset{\equiv C}{\underset{O}{|}}\!>N{\cdot}OH$ is combined with a sufficiently negative radicle.

Hantzsch and Schultze (Abstr., 1896, i, 353, 672) have demonstrated that aqueous solutions of real nitro-compounds have no electric conductivity, whereas a solution of an isonitro-compound conducts the electric current.

Nitrodimethylbarbituric acid is intensely yellow in aqueous solution, and this is caused by the anions; because on adding concentrated hydrochloric acid, which should considerably diminish ionisation, the colour almost entirely disappears. The molecular conductivity of this acid for one gram-molecule dissolved in v litres of water is 313·3 where $v = 32$ and 337·6 where $v = 1024$ (according to Ostwald, μ_∞ should be 352) so that in both dilutions the acid is almost completely ionised, a fact which renders it highly improbable that hydrogen is linked to that carbon atom which has the nitro-group attached to it.

Nitrobarbituric acid in aqueous solution is faintly coloured and has a molecular conductivity 323·4 where $v = 32$, and 341·4 where $v = 512$ (μ_∞ should be 356). Three hydrogen atoms in this acid are replaceable by metals, and when one equivalent of a base is added to its aqueous solution, the colour is not more altered than by adding an equal quantity of water; but the addition of a second equivalent of a base renders the solution intensely yellow. This may be explained by supposing that ionisation of the free acid takes place in such a way that one atom of hydrogen combined with nitrogen becomes the cathion whilst the anion complex (I)  $\begin{array}{l}N\text{——}CO\text{——}NH\\ |\qquad\qquad\qquad\quad |\\ CO{\cdot}C(NO_2)H{\cdot}CO\end{array}$ is itself slowly ionised into H and (II)  $\begin{array}{l}-N\text{—}CO\text{—}NH\\ \;\;|\qquad\qquad\quad |\\ CO{\cdot}CNO_2{\cdot}CO\end{array}$.

This second anion is therefore the cause of the yellow colour; because, as the solution is almost completely ionised, the addition of a first equivalent of a base does not change the colour, for the reason that anion I is present after this addition; but the second equivalent causes almost the entire dissociation of anion I into anion II, and so the colour becomes intense.

The author has been unable to verify von Baeyer's statement that the barium salt of nitrobarbituric acid is not decomposed by sulphuric acid but only by sulphates; on the contrary, precipitation takes place just as well with free sulphuric acid as with potassium sulphate, and from consideration of ionisation, it could not be otherwise.

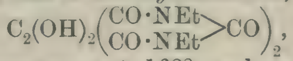
A. W. C.

Malonyldiethylcarbamide and 1 : 3-Diethyluric Acid. By Kurt Sembritzki (*Ber.*, 1897, **30**, 1814—1824).—When diethylcarbamide (11·2 grams) and malonic acid (6·2 grams) are warmed together on the water bath in the presence of phosphorus oxychloride (6 grams) *malonyldiethylcarbamide* (*diethylbarbituric acid*), $\mathrm{CO}<\begin{matrix}\mathrm{NEt\cdot CO}\\ \mathrm{NEt\cdot CO}\end{matrix}>\mathrm{CH_2}$, is formed; the crude syrupy product, weighing 40 per cent. of the theoretical yield, can be used for the subsequent syntheses. (If the three substances are heated in the proportions of 1 mol. of each, *acetylmalonyldiethylcarbamide*, $\mathrm{C_8H_{11}AcN_2O_3}$, melting at 62·5°, is formed.) The pure substance crystallises in rhombic prisms and melts at 52—53°. When shaken with aqueous potassium or sodium nitrite, it forms salts of *diethylvioluric acid*, $\mathrm{CO}<\begin{matrix}\mathrm{NEt\cdot CO}\\ \mathrm{NEt\cdot CO}\end{matrix}>\mathrm{C{:}NOH + H_2O}$, which itself melts at about 90°, or when anhydrous at about 107°. The *sodium* salt, $\mathrm{C_8H_{10}N_3O_4Na, C_8H_{11}N_3O_4 + 2H_2O}$, is brick red; the *potassium* and *ammonium* salts are yellow, and have a similar composition; in the presence of excess of ammonia, a bluish-violet, anhydrous, normal ammonium salt is formed, but this yields the first-mentioned salt when it is recrystallised from water. The barium and lead salts are insoluble, the bluish-black ferrous salt slightly soluble, its solution having a characteristic deep blue colour. It affords a good test for diethylbarbituric acid, one part of which in 10,000 of water can be detected by adding a drop of sodium nitrite and ferrous sulphate, when a blue coloration is produced. When diethylvioluric acid is reduced with hydriodic acid, 1 : 3-*diethyluramil*, $\mathrm{CO}<\begin{matrix}\mathrm{NEt\cdot CO}\\ \mathrm{NEt\cdot CO}\end{matrix}>\mathrm{CHNH_2}$, is formed; this reddens when heated, and melts and decomposes at about 200°. A good way of effecting the reduction is to dilute commercial hydriodic acid, of sp. gr. 1·96, with $\frac{1}{5}$th of its weight of water, cool 10 parts of this diluted acid to − 20°, add 1 part of diethylvioluric acid gradually, shaking meanwhile, and then powdered phosphonium iodide, and continue the shaking, allowing the mixture gradually to attain the ordinary temperature. By heating diethyluramil (1 mol.) in the water bath with potassium cyanate ($1\frac{1}{2}$ mol.) in concentrated aqueous solution, 1 : 3-*diethyl-ψ-uric acid*, $\mathrm{CO}<\begin{matrix}\mathrm{NEt\cdot CO}\\ \mathrm{NEt\cdot CO}\end{matrix}>\mathrm{CH\cdot NH\cdot CO\cdot NH_2}$, is obtained; it melts and decomposes at 196°, and when heated at 100°, with 25 per cent. hydrochloric acid in a flask with reflux condenser, yields 1 : 3-*diethyluric acid*, $\begin{matrix}\mathrm{NEt\cdot CO\cdot C\cdot NH}\\ | \qquad\quad \| \\ \mathrm{CO\cdot NEt\cdot C\cdot NH}\end{matrix}>\mathrm{CO}$, which decomposes gradually when heated above 300°.

Malonyldiethylcarbamide yields *dibromomalonyldiethylcarbamide*,

$$\mathrm{CO}<\begin{matrix}\mathrm{NEt\cdot CO}\\ \mathrm{NEt\cdot CO}\end{matrix}>\mathrm{CBr_2},$$

when it is suspended in water and treated with bromine, and the same product is obtained from diethylvioluric acid; the new compound crystallises in monoclinic prisms [$a : b : c = 1·0284 : 1 : 2·3351$; $\beta = 85°\ 35\frac{1}{2}'$], and melts at 86—87° (corr.). An analogous *chloro*-derivative can be obtained by treating malonyldiethylcarbamide with a little water and strong hydrochloric acid, and adding potassium chlorate gradually; it melts at 87·5° (corr.). When malonyldiethylcarbamide is treated with strong nitric acid, and a drop of fuming nitric acid or a trace of a nitrite added, a part of the product is insoluble in water and cold alcohol, but soluble in hot acetone, is colourless, melts and decomposes at 180° (corr.), and has the composition, $C_{16}H_{20}N_6O_9$. Another product, diethylalloxan, remains dissolved in the water; if this solution is treated with hydrogen sulphide and filtered from sulphur, it deposits colourless crystals of *tetrethylalloxantin*,



$$C_2(OH)_2\left(\begin{matrix}CO\cdot NEt\\CO\cdot NEt\end{matrix}>CO\right)_2,$$

which melts and decomposes at 162°, and can be reconverted into diethylalloxan by cautious oxidation with nitric acid. C. F. B.

Action of Alkaline Hypobromite on Asparagine. By W. VAN DAM (*Rec. Trav. Chim.*, 1897, **16**, 26—32).—According to present views, inactive and active asparagine have the following formulæ, respectively: I. $COOH\cdot CH_2\cdot CH(NH_2)\cdot CO\cdot NH_2$, II. $COOH\cdot CH(NH_2)\cdot CH_2\cdot CO\cdot NH_2$; and therefore, under the influence of alkaline hypobromite, reaction should take place according to the following equations:

$$\text{I.}\quad COOH\cdot CH(NH_2)\cdot CH_2\cdot CONH_2 + KOBr + 3KOH = COOK\cdot CH(NH_2)\cdot CH_2\cdot NH_2 + K_2CO_3 + KBr + 3H_2O$$

(with intermediate production of a bromamide).

$$\text{II.}\quad COOH\cdot CH_2\cdot CH(NH_2)\cdot CONH_2 + KOBr + 3KOH = COOK\cdot CH_2\cdot CH(NH_2)_2 + K_2CO_3 + KBr + 3H_2O.$$

The author has failed to substantiate the above theoretical views, for when natural asparagine is acted on by potassium hypobromite, although the yellow colour of the solution disappears, which would indicate the formation of a bromamide, the latter could not be isolated.

By varying the procedure so as to obtain any $\alpha\beta$-diamidopropionic acid which might have been formed, only the hydrochloride or hydrobromide of aspartic acid was obtained.

Apparently, alkaline hypobromite acts in this case as an oxidising agent, with production of carbonic and oxalic acids; nitrogen being recovered as ammonia.

If excess of hypobromite be used, bromoform is produced, together with the above-mentioned substances. A. W. C.

A New Asparagine. By GIOVANNI SANI (*Rend. Accad. Linc.*, 1895, **4**, ii, 214—217).—On heating a mixture of diethylic fumarate and benzylamine with alcohol at 130—135° in a closed tube for 48 hours, a *substance* of the composition

$$C_7H_7\cdot NH\cdot CO\cdot CH_2\cdot CH(NH\cdot C_7H_7)\cdot CO\cdot NH\cdot C_7H_7$$

is obtained; it crystallises in white flakes melting at 149—150°. On boiling with baryta solution, it gives benzylamine and the crystalline barium *salt* of *dibenzylasparagine*,

$$C_7H_7\cdot NH\cdot CO\cdot CH(NH\cdot C_7H_7)\cdot CH_2\cdot COOH$$

the acid crystallises in scales melting at 204—205°. W. J. P.

Acetodiphosphorous Acid. By HANS VON BAEYER and KARL A. HOFMANN (*Ber.*, 1897, **30**, 1973—1978).—When acetic acid (100 grams) is allowed to remain for 24 hours with phosphorus trichloride (80 grams), the mixture then heated for 1 hour in a reflux apparatus, and finally, after the chloride has been distilled off, for a few minutes at 120—130°, after which the residue is made alkaline with 7 per cent.

aqueous ammonia, ammonium chloride added, and then calcium chloride until the precipitate which forms at first has just disappeared, and the whole heated at 60—70°, *calcium diammonium acetodiphosphite*,

$$C_2P_2O_7H_4Ca(NH_4)_2,$$

eventually separates. If this salt is digested with aqueous silver nitrate, a *calcium silver* salt, $C_2P_2O_6H_3CaAg$, is formed; when it is warmed with aqueous hydroxylamine hydrochloride in the presence of a little alkali, a *calcium dihydroxylamine* salt, $C_2P_2O_7H_4Ca(NH_3OH)_2$, is formed, or a *calcium hydroxylamine* salt, $C_2P_2O_7H_5Ca(NH_3OH)$, if the hydroxylamine is present in great excess. A *manganese ammonium* salt, $C_2P_2O_7H_4Mn(NH_4)_2$, analogous to the calcium ammonium salt, can also be prepared. Further, if the crude product of the reaction described above is half neutralised with sodium carbonate, and ammonium chloride then added in amount rather more than equivalent to the sodium, a *disodium triammonium* salt, $C_2P_2O_7H_3Na_2(NH_4)_3$, is obtained, which contains H_2O after drying in a vacuum over sulphuric acid, and $6H_2O$ when dried over caustic potash in an atmosphere of ammonia. This salt loses $2NH_3$ at 110°, and, with silver nitrate, the residue yields a *silver* salt, $C_2P_2O_7H_5Ag_3$; if its solution is saturated with carbonic anhydride, a *disodium diammonium* salt, $C_2P_2O_7H_4Na_2(NH_4)_2 + 2H_2O$, separates; this loses NH_3 at 110°, and when crystallised from acid solutions yields a *sodium ammonium* salt, $C_2P_2O_7H_6Na(NH_4)$; if it is boiled for a long time with aqueous sodium hydroxide, the very soluble *sodium* salt, $C_2P_2O_7H_3Na_5 + 3H_2O$, separates: a potassium salt analogous to this was also prepared.

These salts are remarkably stable. They do not reduce mercuric, silver, or gold solutions, and they are not decomposed by boiling with nitric acid, aqua regia, or molybdate solution. Fuming nitric acid at 200° does decompose them, however, and so, in great part, does 15 per cent. sulphuric acid at 170°; some phosphoric acid and aldehyde are formed in the latter case. They are oxidised when boiled with aqueous potassium permanganate in the presence of dilute sulphuric acid, some manganese dioxide separating; 1 atom of oxygen is used up for each atom of phosphorus. These reactions are best explained by assigning the formula $OH\cdot CMe[PO(OH)_2]_2$ to the acid; its formation is probably preceded by that of acetylphosphorous acid, $CMeO\cdot PO(OH)_2$, (Menschutkin, *Annalen*, 1865, **133**, 317). C. F. B.

Dithienylethane, Dithienylethylene, and the Condensation of Thiophen with Benzotrichloride and Aluminium Chloride. By Alexander Nahke (*Ber.*, 1897, **30**, 2041—2043).—Phosphoric anhydride (75 grams) is gradually added to a mixture of thiophen (60 grams), monochloracetal (54 grams), chloroform (120 grams) and ether (30 grams), the whole is then warmed for a short time on the water bath and a further quantity (some 40 grams) of phosphoric anhydride is gradually added. After treatment with cold water, the mixture is extracted with chloroform, and the residue left on distilling off the chloroform is purified by distillation in steam at 130—140°. *Dithienylchlorethane* is thus obtained as a yellow oil distilling at 200—205° under a pressure of 25 mm. The same compound may be obtained by the action of phosphoric anhydride on a mixture of thiophen and dichlorether. *Dithienylethylene,* which is formed when the above compound is repeatedly distilled at atmospheric pressure, crystallises from light petroleum in yellowish needles, melting at 125°. *Dithienylethylenic dibromide* melts and decomposes at 128°. *Dithienylbromethane* is a yellow, somewhat fluorescent oil, which distils at 200—210° under 30 mm. pressure, but, at the same time, undergoes partial decomposition. *Dithienyldichlorethane,* obtained from dichloracetal and thiophen, is a colourless oil distilling at 190—195° under 18 mm. pressure; on standing, it solidifies to glistening prisms melting at 32°. When treated with five times its weight of alcoholic potash (12 per cent.), it is converted into *dithienylchlorethylene,* which distils at 170—180° under 23 mm. pressure.

Benzotrichloride and thiophen yield dithienylphenylmethane, and not trithienylphenylmethane. J. J. S.

α-Dithienylethyl Methyl Ketone or Acetyl-α-dithienylethane. By ALEXANDER NAHKE (*Ber.*, 1897, **30**, 2040).—Phosphoric anhydride is added in small portions at a time to a solution of diacetyl (1 molecule) and thiophen (2 molecules) in chloroform, the anhydride being added until a fresh addition causes no further ebullition. After warming for some time on the water bath, water is added, the mixture extracted with ether, and the residue left after removal of the ether is subjected to steam distillation at 150—180°; the oil which passes over with the water, after being extracted with ether, and dried over calcium chloride, is obtained as a lemon-yellow oil boiling at 315—320°. The *hydrazone* is also an oil. J. J. S.

Dithienylphenylmethane—Its Nitro-, Amido-, and Sulphonic Derivatives. By ALEXANDER NAHKE (*Ber.*, 1897, **30**, 2033—2037. Compare Abstr., 1896, i, 690).—Better yields of dithienylphenylmethane, as well as of its three mononitro-derivatives, are obtained when the crude products are purified by distillation with superheated steam, instead of by extraction with dilute alcohol. By this method, 8 grams of dithienylphenylmethane can be obtained from 20 grams of thiophen.

Barium dithienylphenylmethanetrisulphonate,

$$[CH(C_4H_2S\cdot SO_3)_2\cdot C_6H_4\cdot SO_3]_2Ba_3 + 8H_2O.$$

—One to two grams of finely powdered dithienylphenylmethane is intimately mixed with sand which has previously been ignited and washed, and the mixture added to fuming sulphuric acid cooled with ice; the solution is then immediately poured into ice-cold water. When the mixture has been neutralised with barium carbonate, filtered, and the filtrate evaporated, the barium salt is obtained as an amorphous powder containing $8H_2O$; it is readily soluble in water, but practically insoluble in absolute alcohol. The *calcium* salt also contains $8H_2O$. Different salts of the nitro-sulphonic acids have also been prepared.

Dithienylmetamidophenylmethane is obtained as the *stannochloride* by reducing an alcoholic solution of the corresponding nitro-derivative with tin and concentrated hydrochloric acid; this double salt crystallises in needles, and decomposes at 210—220°. The free *base,* which is best obtained by decomposing the above compound with sodium acetate solution, crystallises from light petroleum in needles melting at 73—74°, and dissolving readily in benzene, chloroform, or hot alcohol. The *hydrochloride* also crystallises in colourless needles, which turn red on exposure to the air and decompose at 225—235°. The *platinochloride* crystallises in yellow plates, and the *acetyl* derivative of the base in colourless plates melting at 115°.

Dithienylparamidophenylmethane crystallises in colourless needles melting at 84—85°, and its *hydrochloride* melts at 205—215°. The *acetyl* derivative crystallises in colourless plates, and melts at 142—143°.

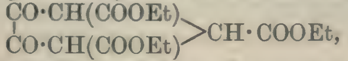
Dithienylorthoamidophenylmethane is best obtained by reducing an alcoholic solution of the nitro-derivative with zinc dust and acetic acid. It crystallises in colourless needles melting at 59—60°, yields a *hydrochloride* and a sparingly soluble *nitrate*, a *platinochloride*, and an *acetyl* derivative melting at 153—154°. The *barium* salts of the three amidotrisulphonic acids are amorphous powders which readily char when heated. J. J. S.

Condensation of Iodothiophen with Benzaldehyde and of Thiophen with different Aldehydes. By ALEXANDER NAHKE (*Ber.*, 1897, **30**, 2037—2039).—Phosphoric anhydride (25 grams) is added to a mixture of iodothiophen (15 grams), benzaldehyde (8 grams), and chloroform (15 grams), and the whole heated on the water bath for 15—30 minutes. When cold, the phosphoric anhydride is hydrolysed with water, and the mixture extracted with chloroform; the residue left after distilling off the chloroform is dissolved in ether, any dark tarry matter is thrown down by vigorously shaking with light petroleum, and the residue from the ethereal solution, after being freed from iodothiophen and benzaldehyde by steam distillation, is crystallised from a mixture of alcohol and ether. The product, *di-iododithienylphenylmethane*, forms small, colourless needles melting at 89°.

Trithienylmethane, obtained by the action of phosphoric anhydride on an ethereal solution of thiophen and thiophenaldehyde, crystallises from light petroleum in colourless needles melting at 49—50°, and is readily soluble in benzene, ether, and hot alcohol. *Dithienylmetatolylmethane* may be obtained in a similar manner from thiophen and metatolualdehyde. It is a pale yellow oil boiling at 210—220° under a pressure of 20 mm. *Dithienylethane*, obtained from thiophen and paraldehyde, is a yellowish oil boiling between 270° and 280°; its odour somewhat resembles that of diphenylmethane. *Dithienylpropane* could not be obtained pure. *Dithienylheptane* is a yellow oil which distils at 200—203° under diminished pressure. J. J. S.

Synthesis of Cyclic Compounds by means of Ethylic Oxalate. By WILHELM WISLICENUS and AUGUST SCHWANHÄUSSER (*Annalen*, 1897, **297**, 98—113).—The formation of ethylic ketipate from ethylic acetate and ethylic oxalate suggested the possibility of producing cyclic systems by the agency of the latter salt. Experiment has now shown that this operation can be successfully performed only in the case of rings containing five carbon atoms; for instance, whilst ethylic oxalate and ethylic tricarballylate yield ethylic diketopentamethylenetricarboxylate, the salt has no ring-forming action on ethylic succinate or ethylic adipate (compare Wislicenus and Boeckler, Abstr., 1895, i, 506).

Ethylic 1 : 2 *diketopentamethylene*-3 : 4 : 5-*tricarboxylate*,



$$\left.\begin{array}{l} CO\cdot CH(COOEt) \\ | \\ CO\cdot CH(COOEt) \end{array}\right> CH\cdot COOEt,$$

is obtained from ethylic oxalate and ethylic propane-$\alpha\alpha_1\beta\beta$-tetracarboxylate (isoallylenetetracarboxylate) under the influence of sodium ethoxide (3 mols.); it crystallises from alcohol in colourless, lustrous prisms, and melts at 122—123°. The salt is insoluble in water, but dissolves readily in alkalis, alkali carbonates, and acetates; the alcoholic solution gives a dark red coloration with ferric chloride. It becomes completely charred when heated, without yielding carbonic oxide, and it cannot be distilled, even under a pressure of 10—15 mm., without undergoing decomposition; the substance is very indifferent towards alkali, and when heated with it in a reflux apparatus becomes brown in part, the remainder being converted into the corresponding alkali derivative; this behaviour prohibits hydrolysis, which, moreover, cannot be effected by hot dilute sulphuric acid, this giving rise to a compound which melts and boils at the same temperatures as diketopentamethylene (Dieckmann, this vol., i, 462), but can scarcely be identical with the latter, as it gives an intense coloration with ferric chloride. If less than three molecular proportions of sodium ethoxide are employed in the preparation of ethylic diketopentamethylenetricarboxylate, the yield is reduced, and a certain amount of *ethylic oxalopropane-$\alpha\alpha_1\beta\beta$-tetracarboxylate* (*oxalisoallylenetetracarboxylate*), $COOEt\cdot CO\cdot CH(COOEt)\cdot C(COOEt)_2\cdot CH_2\cdot COOEt$, is formed; the latter has not been isolated in the purified state, but its identity is established by its conversion, when distilled, into ethylic propanepentacarboxylate, $CH(COOEt)_2\cdot C(COOEt)_2\cdot CH_2\cdot COOEt$, obtained by Bischoff and Emmert from ethylic sodiomalonate and ethylic chlorethanetricarboxylate. Moreover, it develops a red coloration with ferric chloride, and yields ethylic diketopentamethylenetricarboxylate when acted on with sodium ethoxide in excess.

Although, in practice, the employment of ethylic propanetetracarboxylate for the preparation of ethylic diketopentamethylenetricarboxylate is more convenient, the substance is also produced by the action of sodium ethoxide (2 mols.) on a mixture of ethylic oxalate and ethylic tricarballylate. The *disodium* derivative of ethylic diketopentamethylenetricarboxylate forms colourless crystals, containing $3\frac{1}{2}H_2O$, which is lost at 120—130°; the *barium* derivative contains $1\frac{1}{2}H_2O$. The *osazone* crystallises from alcohol in yellow needles, and melts at 163—164°; treatment with a warm solution of ferric chloride produces a deep purple red colouring matter which dissolves in ether. The *tolazine*, $C_{21}H_{24}N_2O_6$, obtained by the action of orthotolylenediamine, crystallises in small needles, and melts at 141—142°.

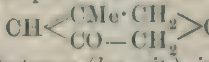
Ethylic oxaladipate, $COOEt\cdot CO\cdot CH(COOEt)\cdot CH_2\cdot CH_2\cdot CH_2\cdot COOEt$, obtained by the action of sodium ethoxide on ethylic oxalate and ethylic adipate, is a colourless oil which develops an intense red coloration with ferric chloride. On attempting to distil it under

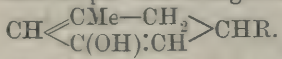
reduced pressure, carbonic oxide is eliminated, and *ethylic adipocarboxylate*, $COOEt\cdot CH_2\cdot CH_2\cdot CH_2\cdot CH(COOEt)_2$, is produced. This is an oil which boils at 192—193° under a pressure of 26 mm., and does not give any coloration with ferric chloride. *Adipocarboxylic acid* melts at 139—140°, when it loses carbonic anhydride, and yields adipic acid.
M. O. F.

Hydrogenised Aromatic Compounds. By EMIL KNOEVENAGEL (*Annalen*, 1897, **297**, 113—137. Compare following abstracts and Abstr., 1896, i, 210).—Further investigation of the synthetical alkyl derivatives of hydrogenised toluene, obtained by reducing certain cycloid ketones (Abstr., 1896, i, 286), has shown that the compounds previously described as tetrahydrophenols or cyclohexenols (*loc. cit.*) are in reality hexahydro-derivatives or cyclohexanols, contaminated with a small proportion of less highly hydrogenised phenols. The fact was revealed on attempting to prepare cyclohexanols by the addition of hydrogen iodide to the supposed cyclohexenols, and submitting the products to reduction with zinc dust and glacial acetic acid. The phenols obtained in this way resembled so closely the original compounds as to suggest identity with them. Careful examination of the substances from this point of view has shown that reduction of the cyclohexenones with sodium and alcohol does actually give rise to the hexahydrophenols, thus emphasising the important fact that saturation of the third ethylenic linking of the benzene ring does not present the difficulty at one time associated with the operation; the experiments may, in fact, be regarded as lending support to Wagner's opinion that one ethylenic group in the carvone molecule is situated in the side chain.

Although, however, the supposed tetrahydrophenols are really hexahydrophenols, and, on oxidation with chromic acid yield hexahydroketones identical with those obtained on oxidising the corresponding hexahydrophenols of known character, the author recognises two series of stereoisomeric hexahydrophenols. Until fresh light is thrown on the question, the hexahydrophenols obtained by reducing cyclohexenones with sodium and alcohol will be referred to as *trans*-cyclohexanols, those obtained from the *trans*-cyclohexanols by treatment with hydrogen iodide, glacial acetic acid, and zinc dust being designated as *cis*-cyclohexanols.

The hydrocarbons obtained from the supposed tetrahydrophenols by the action of phosphoric anhydride must be henceforth regarded as tetrahydro-derivatives of benzene instead of dihydro-compounds.
M. O. F.

Constitution of Cyclohexenones obtained from 1 : 5-Diketones. By EMIL KNOEVENAGEL and A. SCHÜRENBERG (*Annalen*, 1897, **297**, 138—149. Compare Abstr., 1896, i, 210 and 286).—The constitutional formula,  $CH<\begin{matrix}CMe\cdot CH_2\\ CO-CH_2\end{matrix}>CHR$, for the cyclohexenones obtained from 1 : 5-diketones (*loc. cit.*), is based upon their agreement in behaviour with typical ketones, the nature of their products of oxidation, and the relative position of the carbonyl and alkylic groups in the substances employed for their synthesis; the refractive constants, however, uniformly agree more closely with those calculated for substances having the desmotropic enol-configuration,



$$CH\left\langle\begin{matrix}CMe{-}CH_2\\C(OH){:}CH\end{matrix}\right\rangle CHR.$$

In the case of 1-methylcyclohexenone-5, it is probable that the two forms are co-existent, because when the ketone is mixed with water, it is for the most part dissolved, but the undissolved residue is almost insoluble in water; if the soluble constituent is precipitated by potassium carbonate, and its physical properties compared with those of the insoluble portion, the molecular refraction of the former agrees with the calculated value for the enolic form, whilst the latter evidently has ketonic structure. The soluble constituent boils at 199—200°, has a sp. gr. = 0·9726 at 18·5°, and the refractive index $n_D = 1{\cdot}4920$ at 18·5°, whence the molecular refraction $R = 32{\cdot}73$; the insoluble portion boils at 200—201°, has a sp. gr. = 0·9624 at 20·5°, and the refractive index $n_D = 1{\cdot}4711$ at 20·5°, whence the molecular refraction $R = 31{\cdot}88$. The calculated constants for alcohol and ketone are 32·95 and 32·02 respectively.

The *oxime* of 1-methyl-3-isopropylcyclohexenone-5 occurs in two forms, one of which is obtained when the ketone is left in contact with an alkaline solution of hydroxylamine for several days at the ordinary temperature; it crystallises from alcohol, and melts at 88°. The second modification is prepared by treating the ketone with hydroxylamine hydrochloride (2 mols.), and adding a concentrated solution of caustic potash to the cooled liquid until it is feebly alkaline; after many days, water and dilute acetic acid are added, and the product extracted with ether. The oxime crystallises in plates, and melts at 117—118°; the *benzoyl* derivative melts at 155°.

The *phenylhydrazone* of 1-methyl-3-isopropylcyclohexenone-5 forms lustrous, sulphur-yellow crystals, which melt and decompose at about 60°; it becomes darker in the desiccator, and subsequently softens and decomposes.

In attempting to establish the alcoholic character of the cyclohexenones by means of the phenylcarbimide test, it has been shown that it may be applied to tertiary alcohols. The *phenylurethane* of trimethylcarbinol crystallises from ether and melts at 136°. The *phenylurethane* of metamethyldihydroresorcinol crystallises from benzene and melts at 96—97°; the action of heat resolves it into methyldihydroresorcinol and carbanilide. M. O. F.

Stages in the Hydrogenation of Toluene. By EMIL KNOEVENAGEL and J. TÜBBEN (*Annalen*, 1897, **297**, 150—160. Compare Knoevenagel, preceding page; also Abstr., 1896, i, 287 and 310).—cis-1-*Methylcyclohexanol*-5 (*hexahydrometacresol*) is obtained by treating with hydriodic acid dissolved in glacial acetic acid the alcohol formerly described as tetrahydrometacresol, now recognised as hexahydrometacresol contaminated with a small proportion of the tetrahydro-derivative; after 12 hours, the product is reduced with zinc dust, and gently heated on the water bath, the metallic powder being added until iodine is removed from the compound. At this stage, the product contains a large proportion of acetyl derivative, and is therefore hydrolysed with aqueous barium hydroxide; after removal of oxidisable impurities and treatment with sodium hydrogen sulphite, it boils at 174—175° (corr.) under a pressure of 760 mm., sp. gr. = 0·91905 at 16°, and the refractive index $n_D = 1·4579$ at 16°, whence the molecular refraction $R = 33·77$; it is less viscous than the *trans*-modification, is readily volatile in steam, and resembles menthol in odour and taste. The substance is indifferent towards bromine or dilute solutions of potassium permanganate. The *acetyl* derivative has an agreeable, fruity odour, and boils at 193—194° under a pressure of 754 mm.; the *phenylurethane* crystallises from alcohol, and melts at 91°.

5-*Chloro*-1-*methylcyclohexane* is prepared by heating the alcohol with concentrated hydrochloric acid in sealed tubes at 100°; it is a colourless oil of sp. gr. 0·9706 at 15°/4°, and boils at 56—57° under a pressure of 10 mm. 5-*Bromo*-1-*methylcyclohexane* is a colourless, oily liquid, gradually becoming brown when exposed to light; it has a sp. gr. = 1·2543 at 15°/4°, and boils at 70—71° under a pressure of 10 mm. 5 : 1-*Iodomethylcyclohexane* is colourless, but becomes brown under the influence of light; its sp. gr. = 1·5516 at 15°/4°, and it boils at 82—83° under a pressure of 10 mm. (compare Wallach, Abstr., 1896, i, 310).

1-Methylcyclohexanone-5 is prepared by agitating *cis*-methylcyclohexanol with a slight excess of Beckmann's chromic acid mixture; it boils at 169—170° under a pressure of 760 mm., has a sp. gr. = 0 9213 at 19·3°/4°, and the refractive index $n_D = 1·44174$, whence the molecular refraction $R = 32·10$. It is a colourless, mobile liquid, having the taste and odour of peppermint, and is indifferent towards bromine and potassium permanganate solutions. 1-Methylcyclohexanone-5 has also been obtained by Wallach from pulegone and formic acid (Abstr., 1896, i, 309), by Tiemann and Schmidt from the oxime and semicarbazone of isopulegone (Abstr., 1896, i, 383), by the same authors from isopulegone and formic acid (this vol., i, 198), and by Einhorn and Ehret from the distillation of β-methylpimelic acid with soda-lime (this vol., i, 345), whilst Zelinsky and Generosoff have described an isomeride which they obtained from α-methylpimelic acid (Abstr., 1896, i, 350); the constants recorded by the various authors are tabulated in the paper.

Methylcyclohexene (tetrahydrotoluene) is the substance previously described as dihydrotoluene (Abstr., 1896, i, 288); it boils at 105—106° under a pressure of 760 mm., has a sp. gr. = 0·8048 at 20·3°/4°, and the refractive index $n_D = 1·4454$, whence the molecular refraction $R = 31·70$ (compare Wallach, Abstr., 1896, i, 310). The *dibromide* is a colourless liquid which becomes green, and subsequently darkens spontaneously; it boils at 117—118° under a pressure of 117—118 mm., and has a sp. gr. = 1·5718 at 15°/4°.

Methylcyclohexane (hexahydrotoluene), prepared by reducing the iodide of cyclohexanol with zinc dust and glacial acetic acid, boils at 103° under a pressure of 760 mm., has a sp. gr. = 0·7662 at 18·5°/4°, and the refractive index $n_D = 1·41705$, whence the molecular refraction $R = 32·09$. The hydrocarbon is a mobile liquid having the odour of petroleum, and is indifferent towards solutions of bromine and potassium permanganate (compare Zelinsky and Generosoff, Abstr., 1896, i, 351).

M. O. F.

Stages in the Hydrogenation of Metaxylene. By Emil Knoevenagel and MacGarvey (*Annalen*, 1897, **297**, 160—168. Compare foregoing abstract).—cis-1 : 3 *Dimethylcyclohexanol*-5 (*hexahydro*-1 : 3 : 5-*xylenol*) is prepared from the substance previously described as tetrahydro-1 : 3 : 5-xylenol (Abstr., 1896, i, 287) by the action of hydriodic acid, followed by treatment with zinc dust and glacial acetic acid ; it is less viscous than the *trans*-modification (the tetrahydro-derivative in question), and has an agreeable odour suggesting that of menthol. It boils at 187—187·5° under a pressure of 760 mm., has a sp. gr. = 0·9109 at 21°/4°, and the refractive index $n_{\rm D}$ = 1·4540, whence the molecular refraction R = 38·01. The *acetyl*-derivative, which is a mobile liquid having the odour of amylic acetate, boils at 201—202° under a pressure of 748 mm., has a sp. gr. = 0·9226 at 21°/4°, and the refractive index $n_{\rm D}$ = 1·4370, whence the molecular refraction R = 48·21. The *phenylurethane* crystallises from a mixture of alcohol and petroleum, and melts at 110°. 1 : 3-*Dimethylcyclohexanylic*-5 *bromide* boils at 67—69° under a pressure of 6 mm., and at 185—190° under the ordinary pressure, when it undergoes partial decomposition ; it has a sp. gr. = 1·2037 at 15°/4° ; the *iodide*, which has a sp. gr. = 1·4390 at 15°/4°, boils at 92—93° under a pressure of 10 mm., but decomposes when distilled under the ordinary pressure.

1 : 3-*Dimethylcyclohexanone*-5, produced on oxidising *cis*-dimethylcyclohexanol with Beckmann's chromic acid mixture, is a colourless oil, insoluble in water, having the odour of menthol, and is indifferent towards solutions of bromine and potassium permanganate. It boils at 181—182° under a pressure of 760 mm., has a sp. gr. = 0·8994 at 17°/4°, and the refractive index $n_{\rm D}$ = 1·4450, whence the molecular refraction R = 37·31 ; an isomeride has been prepared by Zelinsky (Abstr., 1895, i, 339), by Noyes (Abstr., 1896, i, 696), and by Kipping (Trans., 1895, 349). The *semicarbazone* crystallises from benzene and melts at 190—191°, whilst the *semicarbazone* of 1 : 3-dimethylcyclohexenone-5 (Abstr., 1895, i, 52) melts at 179—180° ; the *oxime* melts at 73°.

Δ^5-1 : 3-*Dimethylcyclohexene* (tetrahydrometaxylene) is the compound previously described as dihydrometaxylene (Abstr., 1896, i, 288) ; it boils at 124—125° under a pressure of 760 mm., has a sp. gr. = 0·8005 at 18°/4°, and the refractive index $n_{\rm D}$ = 1·443, whence the molecular refraction R = 36·43. The *dibromide* is a yellow oil which becomes greenish when kept ; it boils at 105—107° under a pressure of 6 mm., and has a sp. gr. = 1·5390 at 18·5°/4°.

1 : 3-*Dimethylcyclohexane* (hexahydrometaxylene) is prepared by reducing the iodide of 1 : 3-cyclohexane-5. It boils at 120° under a pressure of 760 mm., has a sp. gr. = 0·7736 at 18°/4°, and the refractive index $n_{\rm D}$ = 1·4270, whence the molecular refraction R = 37·06 ; it is identical with Zelinsky's 1 : 3-dimethylhexamethylene (Abstr., 1895, i, 339). A hot mixture of nitric and sulphuric acids converts the hydrocarbons into trinitrometaxylene. M. O. F.

Symmetrical Menthol. By Emil Knoevenagel and G. Wiedermann (*Annalen*, 1897, **297**, 169—174).—cis-1 : 3-*Methylisopropylcyclohexanol*-5 (cis-*symmetrical menthol*) is obtained by the action of hydriodic acid, zinc dust, and glacial acetic acid on the substance previously described as tetrahydro-1 : 3 : 5-carvacrol (Abstr., 1896, i, 287), but consisting really of *trans*-hexahydro-1 : 3 : 5-carvacrol contaminated with a small quantity of less highly hydrogenised alcohol (compare Knoevenagel, this vol., i, 606). It is less viscous than the isomeride, boils at 226—227° under a pressure of 760 mm., has a sp. gr. = 0·9020 at 13·6°/4°, and the refractive index $n_D = 1·46454$ at 13·6°, whence the molecular refraction R = 47·67. It has an agreeable odour suggesting menthol, and is indifferent towards potassium permanganate and bromine. The *acetyl*-derivative boils at 235—236° under a pressure of 752 mm.; the *phenylurethane* crystallises from a mixture of petroleum and alcohol, and melts at 88°. The *chloride* boils at 94—96° under a pressure of 12 mm., decomposing when distilled under atmospheric pressure; it has a sp. gr. = 0·9720 at 14°/4°. The *bromide* has a sp. gr. = 1·1992 at 15°/4°, and boils at 104—106° under a pressure of 12 mm.; the *iodide* has a sp. gr. = 1·4016 at 16°/4°, and boils at 133—134° under a pressure of 12 mm.

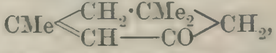
1 : 3-Methylisopropylcylohexanone-5 (*sym*-menthone) is prepared by oxidising *cis*-methylisopropylcyclohexanol with Beckmann's chromic acid mixture; it is a colourless, limpid oil, having a feeble odour of peppermint, and readily forms a crystalline compound with sodium hydrogen sulphite. It boils at 222° under a pressure of 749 mm., has a sp. gr. = 0·9040 at 18°/4°, and the refractive index $n_D = 1·45359$ at 18°, whence the molecular refraction R = 45·98. The *semicarbazone* crystallises from benzene and melts at 176—177°. The *semicarbazone* of 1 : 3-methyl*iso*propylcyclohexenone-5 melts at 166—167°.

1 : 3-*Methylisopropylcyclohexene* (*meta-menthene*), prepared by heating *cis*-symmetrical menthol with phosphoric anhydride at 110—130°, is a colourless, limpid liquid, having the odour of petroleum when freshly distilled, but more closely resembling turpentine after being kept. It decolorises a cold, dilute solution of potassium permanganate and a solution of bromine in chloroform. The substance boils at 169—170° under a pressure of 746 mm., has a sp. gr. = 0·8197 at 16°/4°, and the refractive index $n_D = 1·45609$, whence the molecular refraction R = 45·67. The *dibromide* decomposes when distilled under atmospheric pressure, and boils at 153—155° under a pressure of 19 mm.; it has a sp. gr. = 1·5210 at 16°/4°.

1 : 3-*Methylisopropylcyclohexane* (*meta-menthane*) is obtained by reducing the iodide of symmetrical menthol; it boils at 167—168° under a pressure of 756 mm., has a sp. gr. = 0·8033 at 14°/4°, and the refractive index $n_D = 1·44204$, whence the molecular refraction R = 46·02. It is indifferent towards concentrated sulphuric and nitric acids, and also to solutions of potassium permanganate and bromine. M. O. F.

Corrections regarding Tetrahydrophenols and Dihydrobenzenes. By Emil Knoevenagel and K. Wedemeyer (*Annalen*, 1897, **297**, 175—185).—This paper contains the experimental evidence on which is based Knoevenagel's conclusion that the substances previously described as tetrahydrophenols (Abstr., 1896, i, 287) must be now recognised as hexahydro-derivatives. Particulars are given which relate to the conversion of *cis*- and *trans*-cyclohexanols into cyclohexanones, and it is shown that under the influence of sodium and boiling alcohol *trans*-cyclohexanols are regenerated, thus affording a method of passing from the *cis*- to the *trans*-modification; *trans*-cyclohexanols are converted by phosphoric anhydride into the tetrahydro-derivatives of the corresponding hydrocarbons. M. O. F.

Synthesis and Constitution of Isophorone. By EMIL KNOEVENAGEL and C. FISCHER (*Annalen*, 1897, **297**, 185—203).—1 : 3 : 3-*Trimethylcyclohexenone*-5 (isophorone),



$CMe<\begin{matrix}CH_2\cdot CMe_2\\CH—CO\end{matrix}>CH_2$,

is prepared by treating mesitylic oxide and ethylic acetoacetate with alcoholic sodium ethoxide at the ordinary temperature; after 8 days the liquid is heated on the water bath for 4 hours, hydrolysed with 20 per cent. sulphuric acid, and submitted to distillation in a current of steam. It is identical with the compound described by Fittig (*Annalen*, 1859, **110**, 23), and subsequently by Kerp (Abstr., 1896, i, 447). It boils at 213—214° under a pressure of 760 mm.; it has a sp. gr. = 0·9228 at 18°/4°, and the refractive index $n_D = 1·4766$ at 18°, whence the molecular refraction $R = 42·22$. As in the case of all other cyclohexenones derived from 1 : 5-diketones, therefore, the optical properties are in closer agreement with the enolic formula ($R = 42·16$) than with the ketonic configuration ($R = 41·22$); from a chemical point of view, however, isophorone behaves exclusively as a ketone. It has an agreeable odour of peppermint, and a penetrating, cooling taste; it decolorises solutions of potassium permanganate and bromine immediately in the cold. The *semicarbazone* crystallises in slender, white needles, and melts at 186°; the phenylhydrazone melts at 68—69°. The oxime boils at 134° and 153° under pressures of 16 mm. and 40 mm. respectively, and melts at 74—75° (compare Kerp, *loc. cit.*); the *benzoyl* derivative crystallises in white needles and melts at 99°.

5 : 1 : 3 : 3-*Chlorotrimethylcyclohexadiene* is obtained by adding phosphorus pentachloride to a solution of isophorone in chloroform; it boils at 62° under a pressure of 12 mm., and rapidly becomes brown.

5 : 1 : 3 : 3-*Amidotrimethylcyclohexene* (*isophorylamine*), the base obtained by Kerp on reducing the oxime with sodium and alcohol, boils at 77° under a pressure of 16 mm., and the *hydrochloride* and *benzoyl* derivatives melt at 200° and 122° respectively.

trans-*Dihydroisophorol* (trimethylcyclohexanol) is prepared by reducing isophorone with sodium and alcohol; after distillation, and crystallisation from ether, it melts at 34·5°, and boils at 95° under a pressure of 15 mm., and at 196° under a pressure of 760 mm.; it has a sp. gr. = 0·8778 at 40°/4°. *cis*-Dihydroisophorol is produced when the crude *trans*-modification, which still contains less highly hydrogenised constituents, is treated with hydrogen iodide, and subsequently reduced with zinc dust and acetic acid; it boils at 92° and 201—203° under pressures of 12 mm. and 750 mm. respectively, has a sp. gr. = 0·8096 at 40°/4°, and the refractive index $n_D = 1·4550$, whence the molecular refraction $R = 42·77$. The *acetyl* derivative of both forms boils at 209—210°.

Dihydroisophorone is obtained by oxidising *cis*- and *trans*-dihydroisophorol with Beckmann's chromic acid mixture, and has the odour of peppermint; it boils at 189—190° under a pressure of 752 mm., has a sp. gr. = 0·8923 at 15°/4°, and the refractive index $n_D = 1·4455$, whence the molecular refraction $R = 41·79$. The ketone is indifferent towards solutions of bromine and potassium permanganate, and forms a crystalline *compound* with sodium hydrogen sulphite; the *oxime* and *semicarbazone* melt at 58° and 204° respectively.

1 : 3 : 3-*Trimethylcyclohexene*, is produced by the action of phosphoric anhydride on trimethylcyclohexanol, both modifications of which yield the same hydrocarbon; it is a limpid liquid having the odour of petroleum, boils at 139—141°, has a sp. gr. = 0·7981 at 23°/4°, and the refractive index $n_D = 1·4453$, whence the molecular refraction $R = 41·35$. The hydrocarbon immediately decolorises solutions of bromine and potassium permanganate; it is probably identical with isogeraniolene (Tiemann and Semmler, Abstr., 1894, i, 85).

The *iodide* of dihydroisophorol is obtained by heating *cis*-dihydro-isophorol with hydriodic acid in sealed tubes in the water bath; it is a pale yellow liquid, becoming brown when exposed to light, boils at 97—98° under a pressure of 12 mm., and has a sp. gr. = 1·3804 at 20°/4°.

1 : 3 : 3-*Trimethylcyclohexane* is prepared by reducing the iodide with zinc dust and glacial acetic acid; it boils at 137—138° under a pressure of 760 mm., has a sp. gr. = 0·7848 at 15°/4°, and the refractive index $n_D = 1·4324$ at 15°, whence the molecular refraction $R = 41·68$.

M. O. F.

Derivatives of Cycloheptane. By Eduard Buchner (*Ber.*, 1897, 30, 1949—1950).—By the addition of hydrogen cyanide to suberone and hydrolysis of the product formed, a neutral compound is obtained melting at 130°, and evidently *hydroxycycloheptacarbonamide*,

$$OH\cdot C_7H_{12}\cdot CO\cdot NH_2,$$

which on boiling with hydrochloric acid yields the corresponding hydroxycycloheptanecarboxylic acid (suberylglycollic acid) melting at 79—80°.

J. F. T.

Hexahydrobenzophenone and its Oximes. By Victor Meyer and W. Scharvin (*Ber.*, 1897, 30, 1940—1943).—It was formerly held that oximes containing a fatty and an aromatic group, attached to the carbon atom of the oxime residue, do not exist in two forms because the mobility of the less massive aliphatic radicle enabled the isomerism to escape detection. This is controverted by Claus, in view of the fact that stearophenone, in which the fatty radicle far outweighs the aromatic, yields but one oxime (this vol., i, 187), and an explanation has been put forward by this investigator based on a transformation peculiar to aromatic radicles and becoming apparent when two such groups are present. The authors, however, have observed isomerism in the case of hexahydrobenzophenone, a substance containing only one of those groups in which the rearrangement indicated by Claus could take place. Consequently, the fact that ketoximes containing fatty radicles do not exhibit isomerism remains without explanation.

Hexahydrobenzoic *chloride* boils at 179°, and has a penetrating odour resembling that of benzoic chloride.

Hexahydrobenzophenone, $C_6H_{11}\cdot COPh$, is obtained by treating hexahydrobenzoic chloride with benzene and aluminium chloride; it crystallises from ether and from light petroleum in colourless needles and melts at 54°. The *a-oxime*, obtained from the product by the action of hydroxylamine on the ketone by fractional precipitation with water from its solution in acetic acid, crystallises from alcohol in slender, lustrous needles, and melts at 158°; the *β-oxime*, which is more readily soluble, crystallises in short prisms, and melts at 111°.

Octanoylbenzene (*phenyl heptyl ketone*), $C_7H_{15}\cdot COPh$, is obtained from octoic chloride, benzene, and aluminium chloride; it crystallises in colourless needles, melts at 22°, and boils at 164° under a pressure of 44 mm. The *oxime* crystallises in needles, and melts at 50°; it does not exhibit isomerism. M. O. F.

Condensation of Phloroglucinol with Sugars and Aldehydes. By CONSTANTIN COUNCLER (*Chem. Zeit.*, 1896, **20**, 585—586 and 599).—The condensation product of phloroglucinol and *d*-fructose, previously described (Abstr., 1895, i, 164), is more readily obtained when hydrogen chloride is passed into a mixture of 6 parts of *d*-fructose and 5·4 parts of phloroglucinol suspended in 15 parts of hydrochloric acid (sp. gr. = 1·124). In order to determine, if possible, the constitution of fructosephloroglucide, $C_{36}H_{34}O_{17}$, the author has subjected it to the action of chlorine and bromine. Bromine water acts on a dilute alcoholic solution of the compound, yielding a *bromo*-derivative, $C_{36}Br_{11}H_{23}O_{17}$, which is unstable. A *chloro*-derivative, $C_{36}Cl_{13}H_{21}O_{17}$, can be obtained in a similar manner, and is somewhat more stable; it can only be freed from the last traces of water with great difficulty. Fructosephloroglucide, when kept for some time, loses water and yields the *anhydride*, $C_{72}H_{66}O_{33}$, which is also amorphous and decomposes without melting.

Sorbinose phloroglucide can be obtained as a gelatinous mass, which on drying loses water and yields the *anhydride*, $C_{72}H_{62}O_{31}$. Phloroglucinol also reacts with Lintner's β-hydroxy-δ-methylfurfuraldehyde (Abstr., 1896, i, 144), yielding a condensation product, $C_{24}H_{18}O_9$ or $C_{48}H_{38}O_{19}$.

Phloroglucinol forms condensation products with fatty aldehydes much more readily than with sugars. When phloroglucinol (1 mol.) and the aldehyde (1 mol.) are brought into contact with an excess of hydrochloric acid (12 per cent.), a copious amorphous precipitate is formed. *Formaldehydephloroglucide*, $C_{13}H_{12}O_6$, is best obtained by working in methyl alcoholic solution; it is insoluble in water, but dissolves in alcohol yielding a yellow solution, and begins to decompose at 155°. *Acetaldehydephloroglucide*, $C_{22}H_{22}O_9$, is a golden-yellow precipitate which melts and decomposes at 216°. *Propaldehydephloroglucide*, $C_{33}H_{36}O_{12}$, begins to sinter at 153°. *Isobutyraldehydephloroglucide*, $C_{26}H_{30}O_9$, is a pale rose coloured precipitate melting at 166°. None of the products could be obtained in a crystalline form. They all appear to be formed according to the general equation:

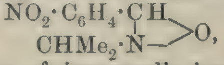
$$mC_nH_{2n}O + (m+1)C_6H_6O_3 = mH_2O + C_{6+m(n+2)}H_{6+2m(n+6)}O_{3(m+1)}$$

J. J. S.

Isomeric Amidines. By REINHOLD WALTHER (*J. pr. Chem.*, 1897, **55**, [ii], 552).—The author as yet sees no reason to doubt the existence of isomeric phenyltolylmethenylamidines (Wheeler, this vol. i, 465). A further paper on the subject will be published.

C. F. B.

β-Substituted Hydroxylamines. By CARL KJELLIN (*Ber.*, 1897, **30**, 1891—1895).—*Isopropylmetanitroisobenzaldoxime*,



$$\begin{array}{l} NO_2\cdot C_6H_4\cdot CH \\ \quad\quad\quad\quad\quad\;\; | \\ \quad\; CHMe_2\cdot N- \end{array}\Big>O,$$

is obtained by the action of isopropylic bromide or iodide on metanitrobenz*syn*aldoxime. It crystallises from benzene in small, yellow prisms melting at 138°, is sparingly soluble in ether, but readily in alcohol or hot benzene, and its ethereal solution gives a white precipitate with hydrogen chloride.

β-Isopropylhydroxylamine hydrochloride, $CHMe_2\cdot NH\cdot OH,HCl$, obtained when the above compound is hydrolysed with concentrated hydrochloric acid, crystallises in large prisms melting at about 55°. The free *base* obtained by treating the hydrochloride with a little less than the theoretical quantity of sodium dissolved in methylic alcohol sublimes in long, silky needles melting at 87°. It is easily soluble in water or alcohol, but only sparingly in benzene or ether. It readily absorbs moisture, reduces Fehling's solution, and is decomposed when strongly heated.

Hydroxyisopropylcarbamide, $NH_2\cdot CO\cdot NPr^{\beta}\cdot OH$, crystallises from water or alcohol in broad needles, melts and decomposes at 104—106°, is insoluble in ether, and gives a reddish-blue coloration with ferric chloride.

Propylmetanitroisobenzaldoxime crystallises in small needles, melts at 65°, and is extremely soluble in alcohol or ether. *Propylhydroxylamine hydrochloride* is an oil, and the free *base* crystallises in white needles melting at 46°; the latter is readily soluble in the usual solvents with the exception of light petroleum.

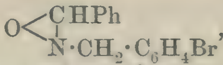
Hydroxypropylallylthiocarbamide, $C_3H_5\cdot NH\cdot CS\cdot NPr\cdot OH$, crystallises in needles and melts at 53—54°; with ferric chloride, it gives a greenish-blue coloration.

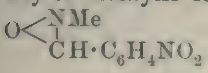
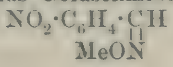
The author has also repeated his work on the action of concentrated hydrochloric acid on β-alkylhydroxylamines (Abstr., 1894, i, 10). In each case, 1—2 grams of the hydroxylamine was heated with three times its weight of concentrated hydrochloric acid for 3 hours at 210—220°. β-Methylhydroxylamine gave ammonia together with a minute quantity of methylamine; β-ethylhydroxylamine gave no ethylamine; β-benzylhydroxylamine gave ammonia and benzoic acid but no benzylamine; orthonitrobenzylhydroxylamine yielded ammonia as the only base. With β-isopropylhydroxylamine, ammonia and mesityl oxide were obtained but no isopropylamine; the mesityl oxide was doubtless formed by the condensation of the acetone liberated in accordance with the following equation

$$CHMe_2\cdot NHOH = COMe_2 + NH_3.$$

J. J. S.

A New Method of Formation of Bisnitrosylbenzyl. By Carl Kjellin and K. G. Kuylenstjerna (*Ber.*, 1897, 30, 1896—1900. Compare Behrend, Abstr., 1891, 1032; 1892, 1199).—When chlorine is passed into a well-cooled aqueous solution of β-benzylhydroxylamine or of its hydrochloride, a greenish, flocculent precipitate is obtained, which, after being washed with water and dried, becomes a white powder melting at 73°. It contains chlorine, and when kept for some time is transformed into a dark coloured oil. When boiled with hydrochloric acid, it yields hydroxylamine, whilst heating with methylic alcohol gives rise to benzaldoxime and bisnitrosylbenzyl melting at 128—129°; a better yield of the latter may be obtained by gradually adding bromine water to a solution of β-benzylhydroxylamine in 50 parts of water. Bisnitrosylparanitrobenzyl may be prepared in a similar manner.

Parabromobenzylisobenzaldoxime,  $\mathrm{O}<\begin{array}{l}\mathrm{CHPh}\\ |\\ \mathrm{N\cdot CH_2\cdot C_6H_4Br}\end{array}$, is formed together with the oxygen ether when *syn*benzaldoxime is alkylated in the usual manner with parabromobenzylic bromide; after recrystallisation from hot alcohol, it melts at 128°. When boiled with 15 times its weight of concentrated hydrochloric acid until all drops of oil have disappeared, it yields *parabromobenzylhydroxylamine hydrochloride* melting and decomposing at 188°. The free *base* is insoluble in water, but is readily soluble in methylic alcohol or hot benzene; it crystallises in small needles melting at about 85°. *Bisnitrosylparabromobenzyl*, $(C_6H_4Br\cdot CH_2\cdot NO)_2$, obtained together with an equal quantity of parabromobenzaldoxime by the action of bromine water on the hydroxylamine, crystallises from hot chloroform in beautiful, short prisms, which melt and decompose at 137—138°. When boiled with alcohol, it is decomposed into the oxime, but it is only slowly hydrolysed by alkalis or by acids. When finely divided and allowed to stand for several days with a 10 per cent. solution of sodium hydroxide, it yields a mixture of *parabromobenz*-syn-*aldoxime* and *parabromobenz*-anti-*aldoxime*; a solution of sodium in methylic alcohol acts much more readily. On passing carbonic anhydride through the diluted alkaline solution the *syn*-aldoxime is first precipitated and then the *anti*-compound can be obtained; whereas if the solution is neutralised with a mineral acid, the *anti*-oxime alone is obtained. The *syn*-aldoxime, which is most readily obtained by intramolecular transformation from the *anti*-compound, crystallises in broad, glistening needles melting at 157°, and is readily soluble in alcohol, benzene, or ether. The *anti*-aldoxime crystallises from light petroleum in colourless needles melting at 108°.

Bisnitrosylorthonitrobenzyl is a white powder melting at 141°; it is more readily acted on by sodium hydroxide than the isomeric parabromo-derivative. An alcoholic solution of sodium ethoxide gives a yellow solution which on treatment with the requisite quantity of methylic iodide yields Goldschmidt and Rietschoten's ethers  $\mathrm{O}<\begin{array}{l}\mathrm{NMe}\\ |\\ \mathrm{CH\cdot C_6H_4NO_2}\end{array}$ and  $\begin{array}{r}\mathrm{NO_2\cdot C_6H_4\cdot CH}\\ \|\\ \mathrm{MeON}\end{array}$ (Abstr., 1893, i, 709).

J. J. S.

Action of Bromine on β-Benzylhydroxylamine and the Constitution of the Bisnitrosylbenzyls. By Carl Kjellin (*Ber.*, 1897, **30**, 1969—1971).—The equation $(x+y)\mathrm{R\cdot CH_2\cdot NH\cdot OH} + (x+y)\mathrm{Br_2} = x\mathrm{RCH{:}N\cdot OH} + \frac{y}{2}(\mathrm{R\cdot CH_2\cdot NO})_2 + 2(x+y)\mathrm{HBr}$ is an exact representation of the action which occurs when a benzylhydroxylamine hydrochloride is treated with bromine, and the author considers that Behrend's formula for the bisnitrosyl compound produced, namely, $\mathrm{RCH_2\cdot N}{<}\begin{matrix}\mathrm{O}\\\mathrm{O}\end{matrix}{>}\mathrm{N\cdot CH_2R}$, is the only one possible. J. F. T.

Action of Furfuraldehyde on Aromatic Hydroxylamines. By Robert Erhardt (*Ber.*, 1897, **30**, 2016—2018).—Furfuraldehyde readily reacts with phenylhydroxylamine in alkaline solution, forming *furfurylidenephenylazoxime*, $\mathrm{C_4OH_3\cdot CH}{<}\begin{matrix}\mathrm{O}\\|\\\mathrm{NPh}\end{matrix}$, which crystallises in white, silky needles melting at 91—92°. It decomposes on exposure to light or when its aqueous solution is boiled for some time. *Furfurylideneorthotolylazoxime* crystallises in large, yellow tablets melting at 58°, and resembles the foregoing compound in its properties. No compound could be obtained with paratolylhydroxylamine.

A. H.

Isomeric Diazoamido-compounds. By Reinhold Walther (*J. pr. Chem.*, 1897, [ii], **55**, 548—552).—The alternative formula proposed by the author for these compounds, is not $\mathrm{NH}{<}\begin{matrix}\mathrm{NR}\\|\\\mathrm{NR}\end{matrix}$, as Hantzsch supposes (this vol., i, 468), but $\mathrm{NR{:}NH{:}NR}$. Objections to it are discussed.

By extracting crude diazoamidobenzene, which melts at 98° or 100° when pure, with cold light petroleum, an isomeride is obtained which melts at 79—80°; if kept at this temperature for a few minutes, it solidifies, and then melts at 90—91°. Further, if dissolved in alcohol and reprecipitated with water, it then melts at 88—93°, and, after a repetition of this treatment, at 97—98°. Possibly this and the ordinary diazoamidobenzene may have the formulæ $\mathrm{NR{:}N\cdot NHR}$ and $\mathrm{NR{:}NH{:}NR}$. C. F. B.

Isomerism of Compounds from Diazonium Salts and Ethylic Acetoacetate. By Carl Kjellin (*Ber.*, 1897, **30**, 1965—1969).—It has already been shown that the compounds formed by the condensation of diazonium chlorides with ethylic cyanacetate always exist in two isomeric forms, and it is now found that the same rule applies, although not to such a marked extent, to compounds derived from the condensation of diazonium chlorides with ethylic acetoacetate. The condensation product of *diazonium chloride* and *ethylic acetoacetate*, $\mathrm{N_2Ph\cdot CHAc\cdot COOEt}$, melts at 80—84°, but on solidifying and remelting melts at 48—60°, and if boiled with alcohol for some time, at 43—50°; the two isomerides could not be separated. The product from *orthochlorodiazonium chloride* and *ethylic acetoacetate*,

$$\mathrm{C_6H_4Cl\cdot N_2\cdot CHAc\cdot COOEt},$$

melts at 80—83°, but on recrystallisation from alcohol the melting point falls to 59—61°; the isomeride of higher melting point is regenerated on treating it with alcoholic potash. With the compound from *parachlorodiazonium chloride*, no isomerism was noticeable; the compound from ethylic *acetoacetate* and sym-*tribromodiazonium bromide*,

$$C_6H_2Br_3N_2\cdot CHAc\cdot COOEt,$$

forms yellow needles melting at 95—109° or 95—113°, which, on fractional recrystallisation from light petroleum, is separated into fractions melting at 121—123° and 117—121° respectively, each of which, on solidifying and remelting, melts at 95—109°.

In the following compounds, no isomerism could be detected.

Metachlorodiazobenzene ethylic acetoacetate, $C_6H_4Cl\cdot N_2\cdot CHAc\cdot COOEt$, which crystallises from light petroleum in dark yellow prisms melting at 70—80°.

Orthobromodiazobenzene ethylic acetoacetate, $C_6H_4Br\cdot N_2\cdot CHAc\cdot COOEt$, forming yellow needles melting at 65—70°.

Orthonitrodiazobenzene ethylic acetoacetate,

$$NO_2\cdot C_6H_4\cdot N_2\cdot CHAc\cdot COOEt,$$

consisting of glistening leaflets melting at 85—95°; the *para-nitro*-derivative crystallises from alcohol in yellow needles melting at 122—123° and the *orthochlorodiazobenzenenitroethane*,

$$C_6H_4Cl\cdot N_2\cdot CHMe\cdot NO_2,$$

in orange-yellow leaflets melting at 112° with decomposition.

J. F. T.

"Hypnoacetin" [Acetophenoneparacetamidophenol]. By G. Vignolo (*Rend. Accad. Linc.*, 1895, 4, i, 358—361).—The author has prepared, by a method which he will publish later, *acetophenoneparacetamidophenol*, $COPh\cdot CH_2\cdot O\cdot C_6H_4\cdot NHAc$; this crystallises in transparent laminæ of pearly lustre melting at 160° with decomposition. The name hypnoacetin is given to it on account of its hypnotic action.

W. J. P.

Iodosobenzoic Acids. By H. Kretzer (*Ber.*, 1897, **30**, 1943—1948).—Diorthiodo-derivatives of benzoic acid, according to the law of etherification, should not yield ethylic salts when treated with alcohol and hydrogen chloride, and, further, should only take up one atom of oxygen on oxidation. Some difficulty was found in the preparation of diorthiodobenzoic acid itself, but the corresponding chlorotri-iodobenzoic acid was found to agree in every way with the above generalisations, and was prepared in the following way. Metamidobenzoic acid, on iodisation, yields *tri-iodamidobenzoic acid*,

$$[COOH : NH_2 : I_3 = 1 : 3 : 2 : 4 : 6],$$

which crystallises from dilute alcohol in colourless leaflets melting and decomposing at 196°; this, on diazotisation, reduction to the hydrazine, and oxidation with ferric chloride, gives 3 : 2 : 4 : 6-*chlorotri-iodobenzoic acid*, which crystallises in glistening plates melting at 226°, and does not yield an ethylic salt on treatment with alcohol and hydrogen chloride.

Chlorodi-iodoiodosobenzoic acid is prepared from chlorotri-iodobenzoic acid by oxidation with potassium permanganate in acid solution, the compound being separated by treating the product with sodium carbonate when the iodoso-acid remains undissolved; it is almost insoluble in water and melts at 206°. The *acid dichloride*, produced on suspending the acid in chloroform and saturating with chlorine, is a yellow powder melting at 204° with evolution of gas; by prolonging the action of the chlorine, the *tetrachloride* is obtained melting at 206° with evolution of gas. J. F. T.

Phenylglycine and Phenylglycineorthocarboxylic Acid: and their Behaviour in the Animal Body. By Jörgen E. Thesen (*Zeit. physiol. Chem.*, 1897, **23**, 23—29).—On account of the ease with which phenylglycine and phenylglycineorthocarboxylic acid can be converted into indoxyl derivatives, experiments were made to ascertain if similar changes take plate in the organism, but without success. In the case of phenylglycine, which is very poisonous to dogs and rabbits, but apparently without toxic effect on frogs, no albumin or sugar appears in the urine. Jaffé's reaction is not more marked and the relative amount of ethylsulphuric acid is not increased. How phenylglycine is secreted could not be definitely proved on account of the very small doses which could be given to animals, and also on account of the few characteristic properties of this substance. With phenylglycineorthocarboxylic acid, which can be given to both dogs and rabbits in large doses without toxic symptoms, the same results were obtained, with the addition of the fact that the unchanged carboxylic acid could be easily detected in the urine.

Indoxylsulphuric acid is synthesised if the product of the fusion of phenylglycineorthocarboxylic acid with caustic potash is treated with potassium pyrosulphate; the residue is then repeatedly extracted with alcohol, and the alcoholic solution concentrated, when amidobenzoic acid separates out. The mother liquor contains the potassium salt of indoxylsulphuric acid, which crystallises from absolute alcohol in white, glistening crystals.

Dibenzylindoxyl, $C_8H_5NO(C_7H_7)_2$, obtained by the action of benzylic chloride on the product of the fusion of phenylglycineorthocarboxylic acid with potassium hydroxide, crystallises from dilute alcohol in yellow crystals melting at 166°. It is insoluble in water but easily soluble in alcohol and ether; its concentrated alcoholic solution is dark red, and the dilute solution has a beautiful green fluorescence. A. W. C.

Action of Alkaline Potassium Hypobromite on certain Amides. Preparation of Methenedioxyamidobenzene. By A. R. Van Linge (*Rec. Trav. Chim.*, 1897, **16**, 44—56. Compare Van Dam, this vol., i, 601).—Piperonylic acid is best prepared by oxidising piperonal with an alkaline solution of potassium hypobromite, when 99 per cent. of the theoretical yield is obtained. When similarly treated, benzaldehyde is converted into benzoic acid and phenanthraquinone into diphenic acid.

Ethylic piperonylate, obtained by saturating a solution of the free acid in alcohol with hydrogen chloride, is a yellow oil, which solidifies to a mass of crystals belonging to the orthorhombic system. It melts at 18·5°, boils at 285·5—286·5°, and is almost insoluble in water, but readily soluble in ether, alcohol, and light petroleum.

Jobst and Hesse have described this substance as an oil boiling between 170° and 200°.

Methylic piperonylate, obtained by a similar method, crystallises in monoclinic needles, melts at 51·5°, and boils at 273—274°.

Piperonylamide is obtained by heating a mixture of methylic piperonylate with aqueous ammonia in sealed tubes at 120°. From dilute alcohol, it crystallises in beautiful, rhombic crystals containing $1H_2O$, and from absolute alcohol in rhombohedral plates. It sublimes without decomposition, is soluble in alcohol and ether, and nearly insoluble in water and light petroleum. By the action of potassium hypobromite in the cold, it is converted into the corresponding *bromamide*; it forms small, white crystals, which readily decompose with evolution of hydrogen bromide.

Methenedioxyamidobenzene, prepared by heating together piperonylamide and an alkaline solution of potassium hypobromite, forms white needles melting at 44°; it is readily soluble in alcohol, ether, chloroform, and carbon tetrachloride, but only sparingly so in water or light petroleum. It decomposes on distillation under diminished pressure, and its aqueous solution, which turns brown on exposure to air, possesses strongly reducing properties, precipitating platinum and silver from solutions of their salts. With calcium hypochlorite, a dilute solution of the base gives a fugitive red, and, with ferric chloride, a dark, violet coloration. The *hydrochloride* is a yellow powder; the *hydrobromide* crystallises in woolly needles; the *nitrate* forms colourless, quadratic plates, decomposing on exposure to moist air and acquiring a red tint; the *sulphate* is obtained as long needles when a concentrated solution of the hydrochloride is treated with ammonium sulphate; the *oxalate* forms rhombic crystals which turn yellow under water; the *picrate* crystallises in yellow needles which decompose with violence when heated, and the *platinochloride* forms small needles, decomposing slowly in the air, and rapidly when heated. The *cadmiochloride* forms colourless crystals. The salts of the base are non-poisonous, and their solutions gradually acquire the property of fluorescing.

The author has studied the action of alkaline potassium hypobromite on the diamides of malonic, succinic, and fumaric acids, in the hope of obtaining amines of the composition $NH_2\cdot CH_2\cdot NH_2$, $NH_2\cdot CH_2\cdot CH_2\cdot NH_2$, and $NH_2\cdot C\vdots C\cdot NH_2$, but without success, as oxidation takes place and the whole of the nitrogen is eliminated as ammonia.

When fumaric bromamide is treated with potassium hypobromite at −2°, maleamide is formed. A. W. C.

Action of Nitric Acid on the Methylamides of Phenylacetic and Phenylpropionic Acids. By H. J. TAVERNE (*Rec. Trav. Chim.*, 1897, 16, 33—43.)—Van Romburgh (*Rec. Trav. Chim*, iv, 384) has shown that when the methyl derivatives of benzamide are treated with nitric acid, a nitro-group enters the combination in the nucleus.

Although the position of the nitro-group with regard to the methylamide group has not been determined, it seems probable, considering the result obtained with benzamide itself, that it would occupy the same positions as in the nitration of benzoic acid, namely, ortho and para.

The methylamides of benzoic acid, on treatment with nitric acid, do not behave like those of acetic acid, which are decomposed under these circumstances; the monomethylamide with production of the nitramide, and the dimethylamide giving nitrodimethylamine. If benzoic acid be looked on as phenylformic acid, and acetic acid as methylformic acid, the difference in the action of nitric acid on their methylamides may perhaps be attributed to the difference in the nature of the methyl and phenyl groups.

The question then arises whether the methylamides of phenylacetic acid compared with those of methylacetic (propionic) acid and also the methylamides of phenylpropionic acid compared with those of methylpropionic (butyric) acid, show the same difference in their behaviour with nitric acid; or, in other words, if the phenyl group, when at a greater distance from the methylamide group, still exercises the same influence. Already, in the nitration of the acids themselves, a difference has been noticed; for whilst benzoic acid gives ortho- and meta- (principally meta-) nitrobenzoic acids, phenylacetic and phenylpropionic acid yield ortho- and para-compounds, and principally the para-compound. As a result of his investigation, the author finds that the methylamides of phenylacetic and phenylpropionic acid react with nitric acid in the same way as those of phenylformic (benzoic) acid, the distance of the phenyl group from the amide group apparently exerting no influence. Although during the nitration of the acids themselves the ortho- and para-nitro-acids are formed, in the case of the methylamide the para-compounds alone are produced. It seems, therefore, that the amide group does exert a certain influence on the reaction.

Phenylacetomethylamide, $CH_2Ph\cdot CO\cdot NHMe$, prepared by the action of methylamine hydrochloride on phenylacetic chloride, is crystalline, melts at 58°, is slightly soluble in water and benzene, and easily soluble in alcohol, ether, and chloroform. By the action of nitric acid, a *nitromethylamide* melting at 156—157° is formed, and this contains the nitro-group in the nucleus, as is proved by treating it with concentrated hydrochloric acid, when paranitrophenylacetic acid is produced. Methylamine is obtained on treating the nitroamide with caustic potash.

Phenylacetodimethylamide, $CH_2Ph\cdot CO\cdot NMe_2$, prepared in a similar manner, is crystalline, melts at 43·5°, and boils at 155° under a pressure of 10 mm. It is easily soluble in ether, chloroform, benzene, and water; and when acted on with nitric acid is converted into a *nitrodimethylamide* melting at 90—91°; dimethylamine is produced when the latter is decomposed with caustic potash, whilst with concentrated hydrochloric acid paranitrophenylacetic acid is obtained.

Phenylpropionomethylamide, $CH_2Ph\cdot CH_2\cdot CO\cdot NHMe$, produced by the interaction of methylamine hydrochloride and phenylpropionic chloride, is crystalline and melts at 59—60°. The corresponding *nitromethylamide* separates from chloroform solution in silken needles melting at 166—167°; when treated with potash, this yields monomethylamine, and with hydrochloric acid, paranitrophenylpropionic acid.

Phenylpropionodimethylamide, $CH_2Ph\cdot CH_2\cdot CO\cdot NMe_2$, is a colourless, syrupy liquid boiling at 162° under a pressure of 10 mm. The *nitrodimethylamide* obtained from it by the action of nitric acid forms acicular crystals melting at 90—91°. With caustic potash, it yields dimethylamine, and with hydrochloric acid, paranitrophenylpropionic acid. A. W. C.

Phthalimide. By JOHN A. MATHEWS (*J. Amer. Chem. Soc.*, 1896, **18**, 679—682).—By heating phthalic acid and propionitrile with a few drops of acetic anhydride in a sealed tube at 180—200°, the author has obtained a 92·5 per cent. yield of phthalimide. E. W. W.

Parachlorobenzonitrile. By L. VAN SCHERPENZEEL (*Rec. Trav. Chim.*, 1897, **16**, 113—115).—*Parachlorobenzonitrile* is prepared by diazotising parachloraniline, and adding the diazo-compound gradually to a solution of copper cyanide, maintaining the temperature at 90°. When the action is ended, the nitrile is distilled with steam.

It crystallises from alcohol in slender, white needles melting at 90°, (which is considerably higher than the melting point of either the ortho- or meta-compound), and boils without decomposition at 223° under a pressure of 750 mm. It is slightly soluble in water and easily so in alcohol, ether, and benzene.

The identity of the substance was proved by converting it into parachlorobenzoic acid, and also into the amide of this acid.

A. W. C.

Peroxides of the Acid Radicles. III. By LUDWIG VANINO (*Ber.*, 1897, **30**, 2003—2005. Compare Abstr., 1894, i, 416; 1896, i, 597).—Benzoic peroxide, which smells like bleaching powder, is not attacked by hydrochloric acid of sp. gr. = 1·19 at 120°, but is decomposed by it at a higher temperature with separation of carbon. Hydrofluoric acid is not affected by it, whilst hydrobromic and hydriodic acids are rapidly oxidised, as is also formaldehyde. The peroxide is only slowly attacked by zinc and hydrochloric acid and by sodium amalgam.

Nitrobenzoic peroxide, melting at 140—141°, can be obtained colourless by repeated crystallisation from alcohol; it is converted by alcoholic ammonia into ammonium nitrobenzoate and by phenylhydrazine into *phenylhydrazine nitrobenzoate*, which melts at 142—143°.

Phthalic peroxide does not appear to yield a nitro-product. None of the organic peroxides oxidise hydrochloric acid, and they are only very slowly acted on by potassium permanganate. A. H.

Benzophenone Derivatives. By PIETRO BARTOLOTTI (*Gazzetta*, 1897, **27**, ii, 18—25).—On heating pyrogallol trimethyl ether with zinc chloride and benzoic chloride at 100° without using a solvent, the principal product is benzoylpyrogallol dimethyl ether,

$$COPh\cdot C_6H_2(OMe)_2\cdot OH,$$

which crystallises in large, yellow prisms melting at 130—131°; a small proportion of benzoylpyrogallol dimethyl ether is formed simultaneously.

Acetylbenzoylpyrogallol dimethyl ether, $COPh\cdot C_6H_2(OMe)_2\cdot OAc$, prepared in the usual way, forms white crystals melting at 104—105°; the corresponding *benzoyl* derivative, obtained by Baumann's method, separates from ethylic acetate in white crystals melting at 111°.

Benzoylpyrogallol trimethyl ether, $COPh\cdot C_6H_2(OMe)_3$, [$COPh : (OMe)_3 = 1 : 2 : 3 : 4$ or $1 : 3 : 4 : 5$], prepared by the action of methylic iodide and soda on benzoylpyrogallol dimethyl ether or of benzoic chloride and zinc chloride in benzene solution on pyrogallol trimethyl ether, is a liquid of high boiling point; on determining the methoxyl in it by Zeisel's method, Graebe and Eichengrün's 1 : 2 : 3-trihydroxybenzophenone is obtained (Abstr., 1891, 706). W. J. P.

Action of Furfuraldehyde on Paradiamines. By ROBERT ERHARDT (*Ber.*, 1897, **30**, 2012—2016).—When tolidine is heated with furfuraldehyde at 100°, condensation occurs and a *difurfurylidene* compound, $C_4OH_3\cdot CH:N\cdot C_6H_3Me\cdot C_6H_3Me\cdot N:CH\cdot C_4OH_3$, is formed, which crystallises in golden-yellow plates, melts at 188—189°, and is readily hydrolysed by heating with dilute acids. Benzidine reacts with furfuraldehyde in a similar manner, yielding a *compound* which crystallises in small, yellow needles melting at 231—232°; this does not appear to be the same as that described by Schiff (Abstr., 1878, 668), since it does not give a carmine red coloration when treated with dilute acid in alcoholic solution. The *compound* obtained from dianisidine forms small, yellow plates melting at 181—182°; like the benzidine compound, it gives with ferric chloride in alcoholic solution a reddish-brown coloration, whilst the tolidine compound gives a yellowish-brown, which becomes olive green on heating. Paraphenetidine also reacts with furfuraldehyde to form a *condensation product*, which is very unstable, but crystallises from ether in yellow tablets melting at 72—73°, and gives a blood-red coloration with ferric chloride in alcoholic solution. It readily unites with bromine and iodine, the compound with the latter element forming a splendid magenta coloured solution in alcohol. A. H.

Stereoisomerism of the Phenylnitrocinnamic Acids. By MARUSSIA BAKUNIN (*Gazzetta*, 1897, **27**, ii, 34—48).—The author has previously described (Abstr., 1895, i, 531) the *trans*-phenylnitrocinnamic acids and, from the mother liquors obtained in their preparation, has isolated the isomeric *cis*- or *allo*-compounds; he now gives further particulars respecting the isomerism of these acids.

Allo-phenylparanitrocinnamic acid melts at 143° and is not converted into the *trans*-isomeride melting at 214° by exposure to diffused light, boiling with iodine, or by adding iodine to the fused substance; the conversion is brought about, however, by several days' exposure to bright sunlight in alcoholic solution, either pure or in presence of iodine or carbon. The *allo*-ortho-acid melting at 147° was not converted into the *trans*-isomeride melting at 195° by iodine. The conversion of the *allo*-meta-acid melting at 195° into the *trans*-acid melting at 181° is hindered by the presence of iodine, but is brought about by exposure to bright sunlight and hastened by the presence of carbon; the incandescent gas light seems incapable of effecting the inter-conversions. The ortho- and para-*trans*-acids do not change into the *allo*-isomerides under the influence of sunlight, but the meta-*trans*-acid in alcoholic solution either alone or, better, in presence of carbon is partially converted into the *allo*-isomeride by direct sunlight.

The *trans*-acids do not combine with aniline, whereas the *allo*-isomerides combine readily with it, giving crystalline salts.

Aniline allophenylorthonitrocinnamate, $C_{15}H_{11}NO_4,NH_2Ph$, crystallises in yellow needles melting at 133°; the meta-*isomeride* crystallises in yellow laminæ melting at 161—162° and the para-*isomeride* melts at 167—168°.

Paratoluidine allophenylorthonitrocinnamate, $C_{15}H_{11}NO_4,NH_2\cdot C_6H_4Me$, crystallises in yellow needles melting at 105°; the *salt* of the meta-acid forms yellow scales melting at 143—144° whilst the *salt* of the para-acid crystallises in yellow needles melting at 181—182°.

Barium allophenylmetanitrocinnamate separates from water in large, transparent crystals containing $4{\cdot}5\ H_2O$ or in aggregates of needles containing $3H_2O$. The *methylic* salt of the *allo*-meta-acid melts at 113—115° and that of the para-acid at 148·5°. The same *amido*-derivative $C_{15}H_{15}NO_2$, which melts at 199—200°, is obtained on reducing both the *allo*- and *trans*-para-acids with sodium amalgam.

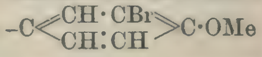
W. J. P.

Stereoisomeric Phenylcinnamic Acids. By MARUSSIA BAKUNIN (*Gazzetta*, 1897, **27**, ii, 48—55).—The most convenient method of preparing the phenylcinnamic acids seems to be to heat together benzaldehyde (10 grams), sodium α-toluate (15 grams) and acetic anhydride (40 grams) at 180°, in an oil bath, for 6 hours; 75 per cent. of the yield is ordinary or *trans*-phenylcinnamic acid melting at 170—172° and the remaining 25 per cent. contains the isomeric *allo*-acid which melts at 136—137°. Stilbene is formed at the same time.

Allo-phenylcinnamic acid gives a *barium* salt which crystallises with $5H_2O$ and $3H_2O$, combines readily with aniline to form a normal salt melting at 128°, and yields a liquid *methylic* salt. The *barium* salt of the *trans*-acid crystallises with $4H_2O$, and the acid does not combine with aniline, but gives a solid *methylic* salt; the *allo*-acid is more soluble in water then the *trans*-acid.

W. J. P.

Dimethylic Ether of Dibromophenolphthalein. By ERNESTO GRANDE (*Gazzetta*, 1897, **27**, ii, 67—70).—By the interaction of orthobromanisol and phthalic chloride, in presence of aluminium chloride, the author has prepared the dibromo-derivative of the dimethylic ether of phenolphthalein which he previously obtained by brominating the ether (Abstr., 1896, i, 563). The dibromo-derivative therefore, contains two groups of the constitution



$-\mathrm{C}{<}\begin{matrix}\mathrm{CH\cdot CBr}\\ \mathrm{CH:CH}\end{matrix}{>}\mathrm{C\cdot OMe}$

and its constitution is fully determined.

The dibromo-derivative dissolves in 5 parts of water at 17°, and when treated with concentrated sulphuric acid gives a yellow crystalline compound which sublimes at 220—230°, contains bromine, and behaves like a hydroxyanthraquinone. When the dibromo-derivative is treated with concentrated hydriodic acid, it gives a mixture of compounds and does not wholly lose its methoxyl.

W. J. P.

Tetraphenylmethane. By MOSES GOMBERG (*Ber.*, 1897, **30**, 2043—2047).—*Triphenylmethane hydrazobenzene*, $CPh_3\cdot NH\cdot NHPh$, is obtained when phenylhydrazine (2 mols.) is added to an ethereal solution of triphenylbromomethane; the ethereal solution, after gently warming on the water bath, is filtered from the precipitate of phenylhydrazine hydrobromide, the filtrate evaporated, and the crystalline residue purified by recrystallisation from benzene or ether. It is a feeble base combining, in ethereal solution, with hydrogen chloride, oxalic acid, picric acid, &c. The melting point is about 135°, but is not sharp, since the compound is readily oxidised to *triphenylmethaneazobenzene*, $CPh_3{\cdot}N{:}NPh$. The latter is most conveniently obtained by suspending the finely divided hydrazo-compound in ether, and adding amylic nitrite and a few drops of acetic chloride, the yellow crystals which separate being recrystallised from alcohol or ether; the yield is good, and the melting point of the azo-compound is 111°. *Tetraphenylmethane* is obtained when the azo-compound is heated above its melting point, or when heated at a lower temperature with copper bronze ("kupferbronze") or platinum sponge.

It can also be obtained by heating a toluene or xylene solution of the azo-compound. The author recommends the following process: triphenylmethaneazobenzene (8 grams) is added in small portions to copper bronze (1 gram) heated at 110°, the molten mass being stirred from time to time; when the evolution of gas has ceased, the residue is extracted with hot benzene, filtered, and the residue left on distilling off the benzene is dissolved in a very little benzene and set aside for 2—3 days. The crystals thus obtained are washed with light petroleum, and then recrystallised several times from benzene. From 8 grams of the azo compound, only 0·3 gram of pure tetraphenylmethane melting at 267·5° (uncorr.) is obtained. The compound is insoluble in ether, acetic acid, or light petroleum, but is readily soluble in hot benzene. J. J. S.

Paradimethylethyloctahydronaphthalene. By AMERICO ANDREOCCI (*Rend. Accad. Linc.*, 1895, **4**, i, 431—435).—On boiling a mixture of santonin, hydrochloric acid, cupric chloride and tin for 10 hours on a sand bath, there is formed, in addition to santonous acid, a paradimethylethyloctahydronaphthalene, $C_{14}H_{24}$, which distils over on heating the liquid, and can be freed from chlorine by boiling with sodium; it boils at 247·4—247·8°, and gives the normal vapour density by V. Meyer's method when heated by diphenylamine vapour in an atmosphere of hydrogen. The crude hydrocarbon contains a little chlorine, owing, probably, to the presence of an additive compound with hydrogen chloride, $C_{14}H_{25}Cl$, which boils at a higher temperature than the hydrocarbon; the hydrocarbon has an odour of mint probably due to contamination with an oxygenated compound. W. J. P.

Puglia Olive Oil. By FRANCESCO CANZONERI (*Gazzetta*, 1897, **27**, ii, 1—5).—The fresh very fruity olive oil from puglia often possesses a markedly bitter taste, and burns the throat; the burning flavour of old rancid oil is somewhat similar to, but quite distinct from, this. The unpleasant flavour (technically termed "raspino") is lost on keeping the oil for some time, and the author has devised a method, which he will describe later, for removing it.

By distilling the oil in a current of steam, the author has separated from it an oil of the nature of camphene, to which olive oil probably owes its characteristic odour and taste, and eugenol, to which the burning flavour is doubtless due. It is noteworthy that Sobrero (*Annalen*, 1845, **54**, 88) obtained eugenol by distilling olivil, $C_{14}H_{18}O_5$. The author has also found catechin, catechol, gallic and tannic acids and a new bitter substance, which in aqueous solution is coloured red by ammonia and violet by ferric chloride, in the faulty oils examined, though not all together in the same sample; the bitter flavour of the oil is attributable to these constituents.

The faulty oils in most, but not in all, cases, give Baudouin's reaction which is supposed to be characteristic of sesame oil; the author finds also that sesame oil does not always give this reaction. W. J. P.

Oil of Basil. By JULIUS BERTRAM and HEINRICH WALBAUM (*Arch. Pharm.*, 1897, **235**, 176—184).—The sample of oil from the island of Réunion possessing a sp. gr. = 0·954 at 15° and a rotatory power = + 10° 12′ (100 mm. tube) was first saponified, and the oil then fractionally distilled. Under 10 mm. pressure, it boils at 75—140°, the largest quantity distilling at 90—93°. In the various fractions, the presence of the following substances was proved. (1) Dextrorotatory pinene in the fraction of low boiling point (by preparing the nitrolbenzylamine compound by Wallach's method). (2) Cineol in the fraction boiling at 175—200°. The hydrobromide and Hirschsohn's iodol compound were obtained. The latter, $C_4I_4NH,C_{10}H_{18}O$, forms yellowish-green crystals, melts at 112°, can be crystallised from alcohol and benzene, is scarcely soluble in light petroleum, and is decomposed by sodium hydroxide with liberation of cineol. (3) Dextrorotatory camphor was found in the fraction which boils at 200—203° by preparing the oxime, and (4) methylchavicol in the large fraction boiling at 90—93°. Under atmospheric pressure, the last named portion boils at 215—216°, has a sp. gr. = 0·969 at 15°, a rotatory power + 5° 57′ (100 mm. tube), and a specific refraction $n_D = 1·51371$ at 20°. This fraction, on oxidation with potassium permanganate, yielded anisic and homoanisic acids, and by treatment with sodium ethoxide, anethoil was prepared, hence the presence of methylchavicol was inferred. The original oil was found to contain 60 per cent. of this compound using Zeisel's methoxy-determination method.

A sample of German oil of basil had a different odour, a sp. gr. = 0·909 at 15° and a rotatory power = − 21° 15′ (100 mm. tube). The presence of cineol was proved, but no camphoroxime could be obtained from the oil. Homoanisic acid was prepared by oxidation, but the oil contained only 24·11 per cent. of methylchavicol. The oil must contain, however, a third alcoholic ingredient, for the fraction boiling at 200° on treatment with acetic anhydride, and subsequent titration with alcoholic potash gave a saponification number which indicated an alcoholic content of 40 per cent. $C_{10}H_{18}O$. This alcohol, in the light of Dupont and Guerlain's work on French oil of basil (this vol., i, 429), is probably linalool. E. W. W.

Isomeric Carvylamines. By HEINRICH GOLDSCHMIDT and ARMIN FISCHER (*Ber.*, 1897, **30**, 2069—2075).—Goldschmidt has shown that on reducing *d*-carvoxime with sodium amalgam, two isomeric carvylamines, $C_{10}H_{17}N$, are produced (Abstr., 1893, i, 723); the authors have examined the reduction products of *l*-carvoxime, and obtained the carbamide and benzoyl derivatives of the optical isomerides of the bases prepared originally. The corresponding racemic compounds have also been examined.

*Benzoyl-α-*d*-carvylamine* melts at 169° (*loc. cit.*); it is lævorotatory, and has $[\alpha]_D = -91{\cdot}9°$. *Benzoyl-β-*d*-carvylamine* has $[\alpha]_D = +176{\cdot}6°$. *Benzoyl-α-*l*-carvylamine* resembles the isomeride, and has $[\alpha]_D = +92{\cdot}6°$. *Benzoyl-β-*l*-carvylamine* has $[\alpha]_D = -175{\cdot}4°$. *Racemic benzoyl-α-carvylamine* crystallises in slender, white needles, melting at 141°, and *racemic benzoyl-β-carvylamine* in small prisms, melting at 140°; the latter is more readily soluble than the α-compound, and a mixture of the two isomerides melts at about 132°. M. O. F.

Constitution of Camphoric Acid. By LUIGI BALBIANO (*Ber.*, 1897, **30**, 1901—1909. Compare Abstr., 1896, i, 493, and this vol., i, 253).—The acid $C_8H_{12}O_5$, obtained from camphoric acid on oxidation, yields the *anhydride* when heated in a sealed tube with acetic anhydride; it is an amorphous substance, and when dissolved in benzene and heated with β-naphthylamine in a reflux apparatus, gives rise to the *β-naphthilic acid*, $COOH{\cdot}C_6H_{10}O{\cdot}CO{\cdot}NH{\cdot}C_{10}H_7$, which crystallises from alcohol in white leaflets, sinters at 168°, and melts and decomposes at 178°.

The acid $C_8H_{12}O_5$ resists the action of hydrochloric acid (sp. gr. = 1·19) when heated with it in sealed tubes at 130—140° during 12 hours; hydrobromic acid (sp. gr. = 1·50), under the same conditions, however, resolves the substance into trimethylsuccinic acid and carbonic oxide, and the same acid is produced under the influence of phosphorus pentachloride and pentabromide on solutions of the substance in phosphorus trichloride and tribromide. Hydrocyanic acid has no action on the compound.

The author summarises his previous work on the acid $C_8H_{12}O_5$, and states reasons for regarding Bredt's formula as an accurate representation of the constitution of camphoric acid. M. O. F.

Active Principles contained in the Bark of Periploca graeca. By EDUARD LEHMANN (*Arch. Pharm.*, 1897, **235**, 157—176).—The author describes in detail the methods used to isolate the bitter principle, *periplocin*, $C_{30}H_{48}O_{12}$, contained in the bark of this plant, which is found in the South-west Caucasus. It forms long, thin, colourless, transparent needles, melts at 205° forming a yellowish, viscous, transparent mass, and decomposes and evolves gas at 215°. It is easily soluble in ethylic and in amylic alcohols. At the ordinary temperature, 1 part dissolves in 125 of water, but it is less soluble in hot water; it is almost insoluble in ether, chloroform, benzene or light petroleum. The specific rotatory power $[\alpha]_D = +20°$. Its colour reactions and behaviour with various reagents are described in detail. On heating the glucoside periplocin with dilute sulphuric acid, *periplogenin*, $C_{24}H_{34}O_5$, is obtained together with a sugar which reduces Fehling's solution, but seems not to be identical with glucose. It is easily soluble in absolute alcohol, 70 per cent. alcohol, and chloroform, less soluble in ether, and insoluble in benzene and light petroleum. Water dissolves only 1 part in 2500, forming a bitter neutral solution. It crystallises in long, monoclinic prisms forming star-shaped groups, is unchanged at 100°, melts at 185° forming a thin, colourless liquid, and decomposes at 200°. The specific rotatory power $[\alpha]_D = +30°$. Its reactions are described in detail. Concentrated nitric acid oxidises both periplocin and periplogenin to a substance probably analogous to trinitrophenol, since its yellow colour is unaffected by alkalis but becomes dark-red on the addition of potassium cyanide.

Attempts to isolate the odoriferous principle of the bark failed.

E. W. W.

Composition of the Root of Baptisia tinctoria. By K. Gorter (*Arch. Pharm.*, 1897, **235**, 301—320).—Baptisin can be extracted from the dried root by means of hot 60 per cent. alcohol, the extract, on evaporation, treatment with sodium hydroxide solution, and shaking with chloroform, yielding large quantities of a white, crystalline substance from which the glucoside can be readily obtained pure by recrystallisation from dilute alcohol. On extraction with chloroform, the alkaline filtrate yielded only small quantities of the alkaloid, but on acidifying the extracted liquid and precipitating with tannin, a second glucoside, *baptin*, was obtained melting at 188—189° after recrystallisation from alcohol. The alkaloid, *baptitoxine*, was obtained from the root, which had previously been extracted with alcohol, by treatment with dilute hydrochloric acid

Anhydrous *baptisin*, $C_{26}H_{32}O_{14}$, melts at 240° (uncorr.), and is lævorotatory $[\alpha]_D = -61° 40'$; it crystallises with $9H_2O$ from dilute alcohol, and on boiling with 16 per cent. sulphuric acid is split up into *baptigenin*, $C_{14}H_{12}O_6$ and rhamnose (isodulcitol); the former crystallises from dilute alcohol in white needles, which become brown at 250° without melting, and on treatment with sodium acetate and acetic acid yield a *triacetyl* derivative, consisting of white needles melting at 214—215° (uncorr.), and on benzoylation by the Baumann-Schotten method, a *monobenzoyl* derivative crystallising from alcohol in slender needles melting at 148°, and a *tribenzoyl* compound also consisting of slender needles melting at 208°. On bromination, baptisin yields a mixture of a dibromo- and a tribromo-derivative, the separation of which was not proceeded with. The presence of methoxy-groups in the glucoside could not be detected.

On nitration, baptigenin yields styphnic acid (trinitroresorcinol), which was identified by the formation of its *naphthalene* compound, which on crystallisation from acetone had the composition

$$C_6H_3N_3O_8,C_{10}H_8 + C_3H_6O;$$

it separates in yellow needles melting at 163·5° (uncorr.); it was not found possible to obtain the compound without acetone of crystallisation. On fusion with potash, both baptisin and baptigenin yield catechol, resorcinol and formic acid, together with a trace of guaiacol, and on oxidation with potassium permanganate, piperonal. When baptigenin is treated with a concentrated solution of sodium hydroxide, it is converted into *baptigenetin*, $C_{12}H_{10}O_4$, which crystallises in glistening, white plates melting at 148° (uncorr.); it is only slightly soluble in cold water, and, on acetylation, yields *diacetylanhydrobaptigenetin*, $C_{12}H_6O_3Ac_2$, a white, crystalline substance melting at 192—194° (uncorr.). None of the compounds above described have any physiological action.

Baptitoxine (cytisine), the alkaloid of the *Baptisia tinctoria*, R. Br, extracted by means of dilute hydrochloric acid, is present in the root in very small quantity. The *nitrate*, $C_{11}H_{14}N_2O,HNO_3 + H_2O$ (cytisine nitrate), crystallises from water in large, yellow crystals; it has a rotatory power $[\alpha]_D = -85° 52'$ at 17°, the free *base* melts at

152—153° (uncorr.) and has a rotatory power $[\alpha]_D = -118° 55'$ at 19°; the *hydrochloride* forms large, white crystals, and the *aurochloride*, which is anhydrous, reddish-brown needles melting at 212—213°.

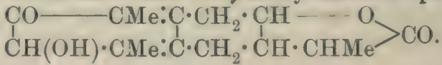
J. F. T.

Constitution of Hydroxysantonin. By D. Lo Monaco (*Gazzetta*, 1897, 27, ii, 87—95).—Jaffé (*Zeit. f. klin. Med.*, 17, Supp., 7, and next abstract) found that santonin, when administered internally to dogs, is eliminated by the urine as a hydroxysantonin, $C_{15}H_{18}O_4$, and showed that this substance still contains the lactonic group present in santonin.

On administering to a dog 1 gram of santonin in meat paste every 24 hours, nothing abnormal is noticed during the first fortnight; after that time, however, the dog becomes emaciated, and each day, after taking the drug, is subject to convulsions of an epileptic nature, which become more intense as time goes on. The urine is yellow, changing to purple when rendered alkaline; the colour disappears after suspending the administration of santonin for 72 hours.

The α-hydroxysantonin separated from the urine is identical with Jaffé's preparation; it gives a *phenylhydrazone*, $C_{15}H_{18}O_3{:}N_2HPh$, which crystallises from boiling alcohol in transparent, yellow scales melting at 264—265°. *Acetyl-α-hydroxysantonin*, $C_{15}H_{17}O_4Ac$, obtained by boiling the santonin with acetic anhydride, crystallises in white scales melting at 164—165°.

The author concludes that α-hydroxysantonin probably has the constitution



$$\begin{array}{l}\mathrm{CO{-\!-\!-\!-}CMe{:}C{\cdot}CH_2{\cdot}CH{-}{-}{-}O} \\ \mathrm{CH(OH){\cdot}CMe{:}C{\cdot}CH_2{\cdot}CH{\cdot}CHMe}\end{array}\!\!>\!\mathrm{CO}.$$

W. J. P.

Hydroxysantonin and its Production from Santonin in the Animal Body. By Max Jaffé (*Zeit. physiol. Chem.*, 1897, 22, 538—555).—From the urine of dogs that have been fed on meat and given from 1—2 grams of santonin daily, *α-hydroxysantonin*, $C_{15}H_{18}O_4$, is obtained by evaporation, and extraction with alcohol. The residue from the alcoholic solution is treated with water and dilute sulphuric acid, and then extracted with ether, from which solvent the hydroxysantonin separates; the yield is from 5—6 per cent. of the santonin given.

α-Hydroxysantonin is sparingly soluble in boiling alcohol, chloroform and ether; slightly soluble in water, forming a neutral solution, and easily soluble in hot glacial acetic acid. From alcohol and chloroform, it separates in colourless, transparent, irregular plates, and from acetic acid in glistening scales which at 286° melt to a dark brown liquid, with disengagement of gas. Its solutions are strongly lævorotatory ($[\alpha]_D = -115°$).

α-Hydroxysantonin remains colourless, or at most becomes slightly yellow, when treated with alcoholic potash, whereas santonin, when similarly treated, becomes deep red; with sulphuric acid, it is coloured yellow, and on adding ferric chloride to the solution it acquires a pale violet colour which becomes clearer on warming, and then changes to a dirty yellowish-brown; the red colour produced with santonin under similar conditions, becomes an intense red-violet on warming.

α-Hydroxysantonic acid is obtained by adding sulphuric acid to a solution of hydroxysantonin in sodium hydroxide. It forms an intensely acid solution, which on warming, and adding a dilute mineral acid, deposits crystals of *a-hydroxysantonic anhydride.* The latter substance readily takes up water to form the free acid, which in strongly alkaline solution has a rotatory power varying from $[\alpha]_D = -128{\cdot}5$ to $[\alpha]_D = -140{\cdot}4°$; and in neutral solution of $[\alpha]_D = -152°$.

The salts of this acid are readily soluble, the addition of soluble barium, calcium, silver, mercuric, and copper salts producing no precipitate. The *cadmium* compound, which appears to be a double salt containing varying amounts of cadmium, crystallises in clusters of needles. The *barium* salt formed by dissolving α-hydroxysantonin in baryta water, is a white powder easily soluble in water and alcohol.

α-Hydroxysantonin is readily oxidised by potassium permanganate or chromic acid, but owing to the small amount of material, the reaction could not be fully investigated, oxalic and hydrocyanic acids being the only substances identified.

On reduction with sodium amalgam, α-hydroxysantonin yields a substance which is probably *hydroxydihydrosantonin*, $C_{15}H_{20}O_4$, in spite of its marked acid character. It is a white powder, which could not be obtained in a crystalline condition; it is insoluble in water, almost so in benzene and light petroleum, but readily soluble in ether and chloroform. When heated in a capillary tube, it softens at 120—150° and changes gradually at 150—170° into a glassy, non-transparent, brown mass. In concentrated sulphuric acid, it dissolves with an intense cherry-red colour, which gradually changes to brown.

By the action of sodium amalgam on santonin, it was found impossible to obtain a compound of definite composition; the product is, however, very similar in properties to the one above described.

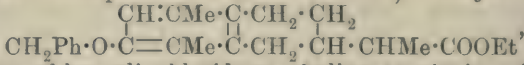
β-Hydroxysantonin, $C_{15}H_{18}O_4$.—Only very small amounts of α-hydroxysantonin could be found in the urine of rabbits to which santonin had been given, but from the ethereal extract the author isolated a new substance which he proposes to call β-hydroxysantonin. It is easily soluble in cold alcohol, ether, and chloroform, but insoluble in light petroleum. Under warm water, it melts to oily drops, which gradually dissolve, and on cooling separate again as plates melting at 128—131°. Its solutions are lævorotatory.

When dissolved in alcoholic potash, β-hydroxysantonin forms an orange-coloured solution, and in dilute sulphuric acid a yellowish-red solution, changing to dark green on addition of ferric chloride. When slowly melted, it changes to a yellow substance, which dissolves in sodium hydroxide with a beautiful red colour, but again turns yellow on acidification. This substance, which it was found impossible to obtain in a pure condition, is probably the yellow colouring matter usually found in urine.

The author suggests that artemisin, obtained by Merck (Abstr., 1896, i, 59) from the seeds of *Artemisia maritima*, as a bye-product in the separation of santonin, may be regarded as *γ-hydroxysantonin.*

A. W. C.

Benzylic Derivaties of the Santonous Acids and of Desmotroposantonin. By NICOLA CASTORO (*Rend. Accad. Linc.*, 1895, 4, ii, 155—163. Compare Abstr., 1896, i, 306).—*Ethylic benzyldextrosantonite*,



$\begin{array}{l} \mathrm{CH{:}CMe\cdot C\cdot CH_2\cdot CH_2} \\ \mathrm{CH_2Ph\cdot O\cdot C{=}CMe\cdot C\cdot CH_2\cdot CH\cdot CHMe\cdot COOEt} \end{array}$

, is prepared by the action of benzylic chloride on ethylic santonite in sodium chloride solution. It is readily hydrolysed by potash, giving the corresponding *acid*, which, although it could not be obtained crystalline, yields a very soluble *sodium* salt crystallising in needles.

Benzyl-levosantonous acid is obtained by reducing benzylisodesmotroposantonin with zinc dust and acetic acid; it does not crystallise, and seems to become racemic when heated at 100° in a vacuum.

W. J. P.

Lapachonone, a new Substance from Lapacho Wood. By F. Crosa and C. Manuelli (*Rend. Accad. Linc.*, 1895, ii, 250—255).—On prolonged distillation in a current of steam, 2 kilos. of lapacho wood yielded a distillate from which 30 grams of a crystalline substance was separated by filtration; the filtrate, on extraction with ether, yielded a few grams of a heavy brown liquid of pronounced odour which boiled at about 180°. This liquid product was not further examined, but the solid, which the authors term *lapachonone*, has the composition $C_{16}H_{16}O_2$; it crystallises in colourless, orthorhombic laminæ melting at 61·5° and the above composition is supported by cryoscopic determinations in benzene and acetic acid. Its solutions are colourless, but rapidly become yellow on exposure to sunlight; if the coloured solutions be kept in the dark, however, they again become colourless. Lapachonone is optically inactive in benzene solution. When crystallised from alcohol with a molecular proportion of picric acid, a *compound* of the composition $C_{16}H_{16}O_2,C_6H_2(NO_2)_3\cdot OH$, melting at 145°, separates, but on recrystallisation from alcohol a new *compound*, of the composition $2C_{16}H_{16}O_2,3C_6H_2(NO_2)_3\cdot OH$, melting at 155°, is deposited, and on again recrystallising, the latter is converted into a *compound* of the composition $C_{16}H_{16}O_2,4C_6H_2(NO_2)_3\cdot OH$ melting at 153°; these substances form almost black, thin needles.

Lapachonone is slowly oxidised by dilute nitric acid, yielding phthalic acid, and is converted into a *dichlorolapachonone*, $C_{16}H_{14}Cl_2O_2$, by treatment with phosphorus pentachloride; the new substance crystallises in large, colourless, monosymmetric prisms melting at 108°, and is volatile in a current of steam.

W. J. P.

Bixin. By Karl G. Zwick (*Ber.*, 1897, 30, 1972).—A preliminary paper, in which the author describes the method he has employed for the preparation of bixin in a crystalline condition.

J. F. T.

Compounds from Lichens. By Oswald Hesse (*Ber.*, 1897, 30, 1983—1989. Compare Abstr., this vol., 1897, i, 255, where, on p. 257, for *Candelaria concolor*, read *Xantharia candelaria*).—*Candelaria concolor* contains no calycin (Zopf, Abstr., 1895, i, 298), but only dipulvic acid. Nor is calycin contained in *Gasparrinia medians* (*Physcia medians, Amphiloma medians*); the compound contained in these lichens resembles rhizocarpic acid, but is distinct from that substance.

The compound obtained, in addition to ethylic hæmatommate, when atranorin is heated with ethylic alcohol, and formerly held (*loc. cit.*) to be methylphysciol, is now shown to be physcianin; as these are the only two products, the formula for hæmatommic acid must be changed to $C_8H_7O_3\cdot COOH$, and atranorin must be regarded as the methylic salt of a lactonic acid, its decomposition by alcohols being represented by the equation

$$\underset{\text{Atranorin.}}{C_{17}H_{15}O_6\cdot COOMe} + R\cdot OH = \underset{\text{Physcianin.}}{C_8H_9O_2\cdot COOMe} + \underset{\text{Alkylic hæmatommate.}}{C_8H_7O_3\cdot COOR}$$

The lichen collected from the bark of the American *Calisaya*, and which contains atranorin ("parmelin") together with a very little vulpic acid, certainly was *Parmelia perlata*; specimens collected at Feuerbach, it is true, contained neither vulpic nor usnic acids. Atranorin further occurs with capraric, physodic, and an amorphous acid in *Parmelia physodes* (*P. ceratophylla*), and with vulpic acid in *Evernia vulpina*; in *E. furfuracea* and *P. stellaris* var. *adscendens*, Th. Fr., it occurs alone.

Caperin and caperidin occur in *P. caperata* collected from the bark of oaks, but not in samples collected from fruit trees or granite rocks. This lichen also contains, in addition to usnic and caperatic acids, *capraric acid*, $C_{24}H_{20}O_{12}$, which crystallises in white needles that darken at 240—260°; it has a bitter taste, contains no alkoxy-group, and yields no acetyl derivative when treated with acetic anhydride, but instead, *anhydrocapraric acid*, $C_{24}H_{18}O_{11}$, which is reconverted into capraric acid by sodium carbonate.

The two compounds obtained by Zopf (this vol., Abstr., 1897, i, 437) from *P. ceratophylla* (*P. physodes*), in addition to atranorin, were probably capraric and physodic acids. Physodic acid, $C_{20}H_{22}O_8$, crystallises in white needles, and melts and decomposes at 190—192°; it contains no alkoxyl group; when boiled with baryta water, it loses carbonic anhydride (1 mol.). Neither capraric nor physodic acid yields ceratophyllin when treated with water, alcohol, or sodium carbonate, so that the atranorin must have been the source of the ceratophyllin (which melts at 147°, not 141°) previously obtained from the lichen in question. Ceratophyllin, physcianin and atraric acid are identical; they are methylic betorcinolcarboxylate. Gerding's physodin, obtained from *P. physodes*, was probably a mixture of atranorin and capraric acid.

Nephromium lusitanicum does not contain emodin, but a yellowish-brown crystalline substance, $C_{16}H_{12}O_6$, melting at 195°, to which the name *nephromin* is given. Presumably, it stands in the same relation to physcion as does emodin to chrysophanic acid. C. F. B.

Constitution of Inorganic Compounds. No. VIII. Anderson's Reaction. By Alfred Werner and Fr. Fassbender (*Zeit. anorg. Chem.*, 1897, 15, 123—142).—The characteristic reaction, known as *Anderson's reaction*, which takes place when the platinochlorides of organic bases are heated, is explained by referring these compounds to the type of metallic ammonium compounds. In the case of the pyridine compounds, the intermediate compound which is formed is a pyridine salt of the acid radicle $PtPyCl_5$. The following results are in accordance with this view.

Pyridine pentachloropyridineplatinate, $HPyPtPyCl_5$, [$Py = C_5NH_5$], a derivative of Anderson's intermediate compound, is easily obtained by warming the aqueous solution of pyridine platinochloride for a short time; it crystallises in large, yellow leaflets. The corresponding alkali salts cannot be obtained in a state of purity by the action of caustic alkalis alone, since the pyridine which is liberated at once reacts with the salts to form the final product of Anderson's reaction. They are, however, easily obtained by gradually adding a solution of the caustic alkali to an alcoholic solution of the pyridine salt containing ten times the theoretical quantity of methylic iodide necessary to combine with the pyridine which is liberated. The *potassium* salt, $KPtPyCl_5$, crystallises from hot water, in which it is easily soluble, in thin leaflets. The molecular conductivity is in accordance with the view that the salt is a compound containing a univalent negative ion. The solution slowly decomposes, and with a dilution of 512 litres after 5 minutes $\mu = 85$, after 480 minutes $\mu = 335$; hydrolysis takes place with the formation of potassium chloride and the acid $PtPyCl_4OH_2$. The *rubidium* salt, obtained in a similar manner to the potassium salt, crystallises from hot water in bright yellow leaflets, which under the microscope are seen to be formed of needles having a vertical fracture and a high double refraction; the solution slowly decomposes in a similar manner to that of the potassium salt. The *cæsium* salt crystallises in microscopic, short, rhombic needles which have a high double refraction. The *sodium* and *lithium* salts, unlike the preceding, contain water of crystallisation, and are easily soluble in alcohol, so that they cannot be prepared by the above method. They are obtained by adding sodium or lithium platinochloride respectively, to a solution of the potassium salt; the filtered solution is then evaporated to dryness and the salt extracted with absolute alcohol. The sodium salt crystallises from water in lustrous, orange-red, rhombic needles, shows a strong double refraction, and is very hygroscopic. The lithium salt crystallises in lustrous, orange-yellow needles.

Trichloropyridine platinites, $MPtPyCl_3$, are obtained by warming pyridine platinosochloride, $Py_2H_2PtCl_4$; they are the compounds corresponding to the above salts in the platino-series.

Potassium trichloropyridineplatinite, $KPtPyCl_3$, is obtained by heating the aqueous solution of pyridine hydrochloride (2 mols.) with potassium platinosochloride (1 mol.) on the water bath until the solution becomes orange-yellow. On concentrating the solution, a mixture of the potassium and pyridine salt is obtained. This mixture is suspended in alcohol, an excess of methylic iodide added, and then a concentrated solution of potassium hydroxide; the sparingly soluble potassium salt thus obtained is washed with alcohol, and crystallised from water, when it is obtained in orange needles having a strong double refraction. The molecular conductivity agrees with that required by the above formula. The aqueous solution, however, quickly undergoes hydrolysis with the formation of potassium chloride and the acid $PtPyCl_2OH_2$. The *rubidium* salt is obtained by adding hydrogen platinochloride to a solution of the potassium salt and adding alcohol; the filtrate which contains the acid $HPtPyCl_3$ is then treated with rubidium chloride, evaporated to dryness, and the residue extracted with water; it crystallises in orange, lustrous needles having a high double refraction. The *cæsium* salt, obtained in a similar manner to the rubidium salt, crystallises in lustrous, orange-yellow, rhombic needles.

The final product of Anderson's reaction is obtained by the action of pyridine on the above compounds. By the action of pyridine on the salts of pentachloropyridineplatinic acid, *platinum-tetrachlorodipyridine*, $PtPy_2Cl_4$, is obtained; this crystallises in small, sulphur-yellow needles. By the action of piperidine, a quantitative yield of the *compound* $PtPyPipCl_4$ is obtained; it is a bright yellow, crystalline powder and is insoluble in water. Platinum-dichlorodipyridine, $PtPy_2Cl_2$, is obtained by the action of pyridine on potassium trichloropyridineplatinite, whilst by the action of piperidine the corresponding *compound*, $PtPyPipCl_2$, is formed.

The reversal of Anderson's reaction takes place easily and a theoretical yield of pyridine platinochloride, Py_2,H_2PtCl_6, is obtained when platinum tetrachlorodipyridine is heated with concentrated hydrochloric acid in a sealed tube at 180°. E. C. R.

3-Hydroxyquinoline-4-sulphonic Acid. By Adolph Claus and Alexander Kaufmann (*J. pr. Chem.*, 1897, [ii], **55**, 509—524. Compare Abstr., 1890, 523).—This acid is the sole product when 3-hydroxyquinoline is sulphonated. The normal *calcium* salt $(OH\cdot C_9NH_5\cdot SO_3)_2Ca + 2H_2O$; *barium*, with $2H_2O$; anhydrous *silver*; *lead*, with $\frac{1}{2}H_2O$; and *cobalt* salt, with $\frac{1}{2}H_2O$, were prepared; also the basic *sodium* salt, $ONa\cdot C_9NH_5\cdot SO_3Na + 1\frac{1}{2}H_2O$, and *potassium* salt, with $1\frac{1}{2}H_2O$. No ethereal salt could be obtained, the action of methylic iodide on the silver salt yielding the free acid and an alkylene, whilst alcoholic hydrochloric acid gives the free acid and the alkylic chloride. The *sulphonic chloride* was obtained as a brown oil which would not solidify; the *sulphonamide* crystallises in white needles and melts at 69—70°. Fusion with potash at 275—280° converts the sulphonic acid into a brown, amorphous substance, which melts and decomposes at about 310°, and is presumably 3 : 4-*dihydroxyquinoline*. Oxidation with potassium permanganate converts the acid into quinolinic (2 : 3-pyridinedicarboxylic) acid; the same product can be obtained by effecting the oxidation with dilute nitric acid, but in this case the sulphonic is certainly first replaced by the nitro-group. When 1 gram of the sulphonic acid is heated with about 20 c.c. of nitric acid of sp. gr. 1·11 for 2 hours in a sealed tube, the main product is nitro-3-hydroxyquinoline if the temperature is 130—140°, quinolinic acid being produced at 150—160°. It was found impossible to introduce any more substituting groups, such as iodine or bromine, into 3-hydroxyquinoline-4-sulphonic acid; the sulphonic group is always removed first. The two bromine derivatives previously described (*loc. cit.*) are now respectively shown to be the yellow *hydrobromide* of *3-hydroxy-4-bromoquinoline* (which itself melts at 186°), and a mixture of this with unchanged sulphonic acid, from which it is not easily freed. C. F. B.

Methyl-loretine and Lorenite. By Adolph Claus and Adolph Kaufmann (*J. pr. Chem.*, 1897, [ii], **55**, 524—541).—*Methyl-loretine*

(*2-iodo-1-hydroxy-3-melthylquinoline-4-sulphonic acid*) is prepared by the following series of reactions: $C_9NH_6Me \rightarrow SO_3H\cdot C_9NH_5Me \rightarrow OH\cdot C_9NH_5Me \rightarrow OH\cdot C_9NH_4Me\cdot SO_3H \rightarrow OH\cdot C_9NH_3IMe\cdot SO_3H$. It crystallises with $1H_2O$, decomposes at 185—220° when heated, and is, generally, decidedly less stable than loretine itself; when oxidised with permanganate, it yields 2:3-pyridinedicarboxylic acid. The *sodium* salt, $OH\cdot C_9NH_3IMe\cdot SO_3Na$, also the *potassium*, with $\frac{1}{2}H_2O$; *ammonium*; *calcium*; *barium*, with $1H_2O$ (with $3H_2O$ when air-dried only?); and *strontium* salts, with $1H_2O$, were prepared. The basic salts of the same metals (except ammonium), $ONa\cdot C_9NH_3IMe\cdot SO_3Na$, &c., were likewise obtained; of these, the potassium salt crystallises with $\frac{1}{2}H_2O$, whilst the others are anhydrous. The normal salts are orange-coloured, and decompose at about 160—170°; the basic salts decompose at about 270—300°, and are colourless.

Lorenite (*3-iodo-4-hydroxyquinoline-1-sulphonic acid*) is prepared by sulphonating 4-hydroxyquinoline and iodising the product. It is isomeric with loretine, and resembles it, rather than methyl-loretine, in the degree of its stability; it decomposes at 210—230°; its normal salts are red and decompose between 190° and 250°, whilst the basic salts decompose at a higher temperature and are colourless or yellowish-white. The normal *sodium* (with $5H_2O$ when air-dried?); *potassium*, with $2H_2O$; *calcium*, with xH_2O; *barium*; and *strontium* salts, with xH_2O, were prepared; also the corresponding basic salts, with respectively 4, x, 4, O, and xH_2O.

When either loretine, methyl-loretine, or lorenite is applied externally as a drug, no iodine is present in the urine; it is found, however, in the form of both iodides and organic iodine derivatives when either of these drugs is taken internally, and its presence is indicated by the liberation of iodine when nitric acid is added to the urine. In order to liberate all the iodine from loretine or methyl-loretine, 6—8 times as much nitric acid must be used as will liberate completely the same amount of iodine present originally in the form of a metallic iodide.

C. F. B.

Ethylic Dicarboxylglutaconate. By SIEGFRIED RUHEMANN and A. S. HEMMY (*Ber.*, 1897, **30**, 2022—2031. Compare Trans., 1891, 743).—When ethylic dicarboxyglutaconate is treated with an excess of benzylamine, *ethylic benzylamidoethylenedicarboxylate*,

$$CH_2Ph\cdot NH\cdot CH\colon C(COOEt)_2,$$

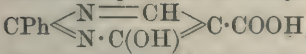
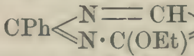
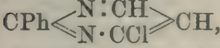
is produced, and crystallises in colourless prismatic plates melting at 73—74°. Diethylamine unites with ethylic dicarboxyglutaconate to form a *salt*, $CH(COOEt)_2\cdot CH\colon C(COOEt)_2,NHEt_2$, which crystallises in yellow needles and decomposes at 130°. When heated with diethylamine at 100°, *ethylic diethylamidoethylenedicarboxylate*,

$$NEt_2\cdot CH\colon C(COOEt)_2,$$

is produced, which is a yellow, ethereal oil, of sp. gr. = 1·0435 at 28°/28°, and boils at 188° under a pressure of 15 mm. Piperidine behaves in a similar manner, forming a yellow, crystalline salt, which when heated with piperidine yields *ethylic piperidylethylenedicarboxylate*, as a viscid, yellow oil boiling at 223—224° under a pressure of 16 mm. Paraphenylenediamine reacts with ethylic dicarboxyglutaconate in the same mannner as metaphenylenediamine (Abstr., 1895, i, 334), *ethylic paraphenylenediamidodiethylenetetracarboxylate*, $C_6H_4[NH\cdot CH{:}C(COOEt)_2]_2$, being produced, which crystallises in yellowish-green, silky needles melting at 164—165°. Orthophenylenediamine, on the other hand, only reacts with 1 molecule of the ethylic salt, *ethylic orthophenylenediamidoethylenedicarboxylate*,

$$NH_2\cdot C_6H_4\cdot NH\cdot CH{:}C(COOEt)_2,$$

being formed. It crystallises in faintly yellow prisms melting at 92—93°. *Ethylic a-orthotolylenediamidoethylenedicarboxylate*, is obtained in a similar manner and crystallises in yellowish prisms melting at 145—146°.

The phenylpyrimidone melting at 207—208° (phenylhydroxypyrimidine), obtained by Ruhemann and Hemmy (this vol., i, 488) by the decomposition of 4-hydroxy-2-phenylpyrimidine-5-carboxylic acid,  $\mathrm{CPh}{<}\genfrac{}{}{0pt}{}{\mathrm{N{=\!=}CH}}{\mathrm{N\cdot C(OH)}}{>}\mathrm{C\cdot COOH}$, should be identical with that obtained by Pinner from 6-hydroxy-2-phenyl-4-carboxylic acid (*Die Imidoäther*, Berlin, 1892, 257), although the latter gave the melting point as 199°. The following derivatives may serve to characterise this compound more fully. 4-*Ethoxy-2-phenylpyrimidine*,  $\mathrm{CPh}{<}\genfrac{}{}{0pt}{}{\mathrm{N{=\!=}CH}}{\mathrm{N\cdot C(OEt)}}{>}\mathrm{CH}$, is readily obtained by the action of ethylic iodide on the hydroxy-compound, and forms a colourless oil which boils at 180° under a pressure of 24 mm., has the sp. gr. $=1{\cdot}1204$ at 19°/19°, and possesses a blue fluorescence. It forms a colourless, crystalline *hydrochloride* and a *platinochloride* which decomposes at 200°. 4-*Chloro-2-phenylpyrimidine*,  $\mathrm{CPh}{<}\genfrac{}{}{0pt}{}{\mathrm{N{:}CH}}{\mathrm{N\cdot CCl}}{>}\mathrm{CH}$, obtained by the action of phosphorus pentachloride on the hydroxy-compound, crystallises in colourless plates melting at 74°; it dissolves in concentrated hydrochloric acid, and yields a yellow, crystalline *platinochloride*, $(C_{10}H_7N_2Cl)_2,H_2PtCl_6$. Alcoholic ammonia at 150° converts the chloro-derivative into 4-*amido-2-phenylpyrimidine*, which crystallises with $\frac{1}{2}H_2O$ in colourless, compact prisms, and melts at 138—139° after losing its water at 120°; the anhydrous compound forms an amorphous mass, which takes up water from the air. The *hydrochloride* is readily soluble, and the *platinochloride* decomposes at 225°. The *acetyl* derivative crystallises in prismatic plates melting at 174—175°, and yields a *platinochloride*, which decomposes at 258°. The *benzoyl* derivative crystallises in colourless plates melting at 141°, and is insoluble in dilute acids.

A. H.

Cumenylimido-ethers. By PHILIPP FLATOW (*Ber.*, 1897, 30, 2006—2010).—*Cumenylimidoethyl ether hydrochloride*,

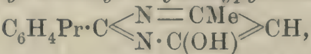
$$C_9H_{11}\cdot C(OEt){:}NH,HCl,$$

is formed when paracuminonitrile is treated with alcoholic hydrogen chloride. It melts at 98°, ethylic chloride being evolved and cuminamide produced, which then solidifies and melts again at 150°. All attempts to prepare the free imido-ether were unsuccessful.

Cumenylimidopropyl ether hydrochloride crystallises in slender, yellow, needles, which melt and decompose at 108°.

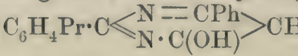
Cumenylamidine hydrochloride, $C_9H_{11}\cdot C(NH_2)\colon NH,HCl$, is produced by the action of alcoholic ammonia on the hydrochloride of the imidoether, and crystallises in colourless tablets which melt at 190°. The *platinochloride* melts at 210°, the *picrate* at 195°.

2-*Paraisopropylphenyl*-4-*methyl*-6-*hydroxypyrimidine*,

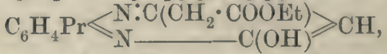


$$C_6H_4Pr\cdot C{<}\begin{matrix}N = CMe\\ N\cdot C(OH)\end{matrix}{>}CH,$$

obtained by treating cumenylamidine hydrochloride with caustic soda and ethylic acetoacetate, crystallises in colourless needles which melt at 165°, and are soluble both in acids and alkalis.

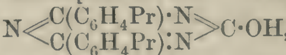
6-*Hydroxy*-2-*paraisopropylphenyl*-4 : 5-*dimethylpyrimidine*, which is prepared from ethylic methylacetoacetate, crystallises in long, silky needles melting at 208°. 6-*Hydroxy*-2-*paraisopropylphenyl*-4-*phenylpyrimidine*,  $C_6H_4Pr\cdot C{<}\begin{matrix}N = CPh\\ N\cdot C(OH)\end{matrix}{>}CH$, forms thin, silky needles melting at 227°.

Ethylic 6-*hydroxy*-2-*paraisopropylphenylpyrimidine*-4-*acetate*,

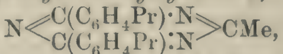


$$C_6H_4Pr{<}\begin{matrix}N\colon C(CH_2\cdot COOEt)\\ N\text{———}C(OH)\end{matrix}{>}CH,$$

is prepared by the use of ethylic acetonedicarboxylate, and crystallises in long, thin, silky needles melting at 128°.

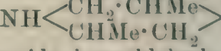
6-*Hydroxy*-2-*paraisopropylphenylpyrimidine*-4-*carboxylic acid* is prepared from ethylic oxalacetate, and separates from alcohol in small scales which melt and decompose at 266°. 6-*Hydroxy*-2 : 4-*diparaisopropylphenylcyanidine*,  $N{<}\begin{matrix}C(C_6H_4Pr)\cdot N\\ C(C_6H_4Pr)\colon N\end{matrix}{>}C\cdot OH$, obtained by the action of phosgene on the amidine, crystallises in yellowish plates, with a satiny lustre, and melts at 253°.

2 : 4-*Diparaisopropylphenyl*-6-*methylcyanidine*,



$$N{<}\begin{matrix}C(C_6H_4Pr)\cdot N\\ C(C_6H_4Pr)\colon N\end{matrix}{>}CMe,$$

is formed by the action of acetic anhydride on the amidine. It crystallises in slender needles and melts at 68°. A. H.

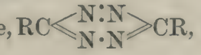
Existence of Condensation Rings with Para-linkage. By Franz Feist (*Ber.*, 1897, 30, 1982—1983. Compare Ladenburg, this vol., i, 485).—The author was unable to obtain a para-linkage by treating 2 : 5-dimethylpiperazine,  $NH{<}\begin{matrix}CH_2\cdot CHMe\\ CHMe\cdot CH_2\end{matrix}{>}NH$, with ethylenic iodide or bromide, stilbene bromide, benzaldehyde, formaldehyde, carbonyl chloride, or carbon bisulphide. In the last case, the product was the bisdithiocarbamate, $C_4N_2H_6Me_2(CSSH)_2$, which melts at 205°; this forms no para-linking when treated with ethylenediamine, neither does the dinitrosamine, when reduced; the dinitramine, curiously enough, yields the dinitrosamine when it is allowed to remain in contact with acetic anhydride. C. F. B.

Action of Phosphorus Chloride on Rosindone and Aposafranone. By Otto Fischer and Eduard Hepp (*Ber.*, 1897, 30, 1827—1831).—When rosindone (1 mol.), dissolved in five times its weight of phosphorus oxychloride, is treated with phosphorus pentachloride (1 mol.), the product is a reddish-yellow, crystalline substance, with metallic lustre. This substance is readily decomposed by alkalis, and even by aqueous sodium acetate, rosindone being regenerated; when it is treated with potassium bromide or iodide, chlorine (? 1 atom) is displaced by bromine or iodine, whilst potassium nitrate throws down a sparingly soluble nitrate; with gold and platinum chlorides, it yields respectively a reddish-yellow *aurochloride* and a yellow *platinochloride*, both of which are anhydrous. It has thus the character of a salt, and must be regarded as *chloronaphthophenazonium chloride*,

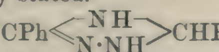
$$C_{10}H_5Cl<\genfrac{}{}{0pt}{}{N}{NPhCl}>C_6H_4,\ [N:N:Cl=1:2:4].$$

With aniline in alcoholic solution, it yields phenylrosinduline, and with ethylamine and methylamine respectively it yields ethylrosinduline and *methylrosinduline*; the last, $C_{23}H_{17}N_3$, melts at 180—181°; all of them have a greenish surface lustre.

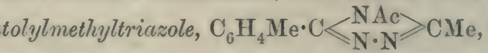
Aposafranone, when treated in a similar fashion, yields *chlorophenylphenazonium chloride*, $C_6H_3Cl<\genfrac{}{}{0pt}{}{N}{NPhCl}>C_6H_4$, $[N:N:Cl=1:2:4]$. This forms brownish-yellow crystals with a bluish surface lustre, and resembles the compound described above in its chemical properties. With aniline, it yields *phenylaposafranine*, $C_{24}H_{17}N_3$, which crystallises in dark prisms with a bronze-like lustre, and melts at 201°. C. F. B.

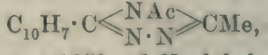
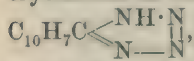
Action of Hydrazine on Imido-ethers. By ADOLF PINNER (*Ber.*, 1897, **30**, 1871—1890. Compare Abstr., 1893, i, 710; 1894, i, 385; 1895, i, 136 and 270).—As a rule, the following compounds can be isolated from the products obtained by the action of hydrazine on an imido-ether, $R'O{\cdot}CR{:}NH$. (1)—The monhydrazidine, $NH_2{\cdot}CR{:}N{\cdot}NH_2$, obtained by the direct addition of hydrazine to the imido-ether and the subsequent elimination of a molecule of alcohol. (2)—The dihydrazidine, $NH_2{\cdot}CR{:}N{\cdot}N{:}CR{\cdot}NH_2$, formed by the addition of a molecule of the imido-ether to the monhydrazidine, and the subsequent loss of a molecule of alcohol. (3)—The dihydrotetrazine, $RC<\genfrac{}{}{0pt}{}{NH{\cdot}NH}{N\text{——}N}>CR$, formed by the action of free hydrazine on the monhydrazidine. (4)—The dihydrotriazole, $RC<\genfrac{}{}{0pt}{}{NH}{N{\cdot}NH}>CHR$, formed by the oxidation of the monhydrazidine, water, nitrogen, and ammonia being liberated. (5)—The triazole, $RC<\genfrac{}{}{0pt}{}{NH}{N{\cdot}N}>CR$, formed at the expense of the dihydrazidine. (6)—The tetrazine,  $RC<\genfrac{}{}{0pt}{}{N{:}N}{N{\cdot}N}>CR$, formed by the oxidation of the dihydrotetrazine. (7)—The isodihydrotetrazine, $RC<\genfrac{}{}{0pt}{}{NH{\cdot}N}{N{\cdot}NH}>CR$, obtained by the intramolecular transformation of the dihydrotetrazine.

Acetic anhydride and sodium acetate react with dihydrazidines, yielding triazoles and acetyltriazoles, and not the true acetyl derivatives of the dihydrazidines as previously stated.

2 : 5-*Diphenyldihydrotriazole*,  $CPh<\genfrac{}{}{0pt}{}{NH}{N{\cdot}NH}>CHPh$, is the compound previously (Abstr., 1893, i, 711) described as dibenzimidine. It is readily soluble in alcohol and acetone, extremely sparingly in water

and melts at 137°. It possesses somewhat strong basic properties, and its *hydrochloride* and *nitrate* are sparingly soluble in cold water. The *diacetyl* derivative, $C_{14}H_{11}N_3Ac_2$, obtained by boiling the base with sodium acetate and acetic anhydride for several hours, crystallises from light petroleum in short, thick prisms, melts at 93°, and is readily soluble in most organic solvents. When diphenyldihydrotriazole is heated with hydrochloric acid (10—12 per cent.) for several hours at 100° and then at 150°, it is converted into a mixture of benzoic acid, benzaldehyde, and Curtius's benzalazine, $CHPh\cdot N\colon N\cdot CHPh$.

1 : 5 : 2-*Acetylparatolylmethyltriazole*,  $C_6H_4Me\cdot C{<}\substack{NAc\\ N\cdot N}{>}CMe$, is obtained when tolenylhydrazidine hydrochloride is added to a hot mixture of sodium acetate (2 parts) and acetic anhydride (12 parts), and the whole is heated for an hour; it crystallises in transparent prisms melting at 112°, and is readily soluble in hot alcohol. When tolenylhydrazidine hydrochloride is boiled for 10—15 minutes with a large excess of formaldehyde, and the mixture is allowed to cool, *tolenyldimethylenehydrazidine*, $CH_2\colon N\cdot C(C_6H_4Me)\colon N\cdot N\colon CH_2$, separates in glistening needles melting at 193°.

[With ALFRED SALOMON.]—When free hydrazine ($1\frac{1}{2}$ mol.), obtained by the action of caustic potash (33 per cent.) on hydrazine sulphate, is mixed with β-naphthimido-ether hydrochloride and alcohol (a quantity equal to the water present), the mixture sets to a mass of crystals which can be separated after 24 hours, and the β-naphthenylhydrazidine freed from potassium sulphate and chloride by treatment with dilute hydrochloric acid, extracting any unaltered imido-ether with ether, and then rendering the acid solution alkaline. *β-Naphthenylhydrazidine*, $NH_2\cdot C(C_{10}H_7)\colon N\cdot NH_2$, which crystallises in yellowish plates, is only sparingly soluble in water, but dissolves readily in alcohol, acetone, and acids; it begins to melt at 160°, but immediately solidifies, and then melts again and decomposes at about 230°. The *picrate* crystallises in yellow needles melting at 202°. *β-Naphthenyldimethylenehydrazidine*, $CH_2\colon N\cdot C(C_{10}H_7)\colon N\cdot N\colon CH_2$, melts and chars at 277°. *β-Naphthenylbenzylidenehydrazidine*, $NH_2\cdot C(C_{10}H_7)\colon N\cdot N\colon CHPh$, which crystallises in flat, yellowish needles melting at 96°, yields a *picrate* also crystallising in yellow needles. *β-Naphthenylcinnamylenehydrazidine*, $NH_2\cdot C(C_{10}H_7)\colon N\cdot N\colon CH\cdot C_8H_7$, melts at 170°, and yields a *picrate* melting at 180°. The monhydrazidine when heated with acetic anhydride yields *naphthoylhydrazide*, $C_{10}H_7\cdot CO\cdot NH\cdot NH_2$, crystallising in needles and melting at 186°. When a mixture of acetic anhydride and anhydrous sodium acetate is used, the chief product is 1 : 5 : 2-*acetyl-β-naphthylmethyltriazole*,  $C_{10}H_7\cdot C{<}\substack{NAc\\ N\cdot N}{>}CMe$, which crystallises in colourless needles melting at 135°. *β-Naphthyltetrazole*,  $C_{10}H_7C{<}\begin{matrix}NH\cdot N\\ \quad\ \|\\ N{-}{-}N\end{matrix}$, prepared by adding sodium nitrite to a solution of the hydrazidine hydrochloride, crystallises in colourless prisms melting and decomposing at 203°. It is readily soluble in alcohol, ether, or acetone, yields an *ammonium* derivative, $C_{11}H_7N_4\cdot NH_4$, crystallising in colourless plates and melting at 210°, also *lead*, *silver*, *methyl*, and *ethyl* derivatives, the last two melting at 112° and 55° respectively.

Dinaphthenylhydrazidine, $NH_2\cdot C(C_{10}H_7){:}N\cdot N{:}C(C_{10}H_7)\cdot NH_2$, is the chief product obtained by the action of hydrazine (1 mol.) on naphthimido-ether (1½ mol.). It is only sparingly soluble in the usual solvents, but crystallises from aniline in yellow, glistening plates; it melts at 246°, but is converted at the same time into the tetrazole. It possesses very feeble basic properties; when suspended in acetone and treated with concentrated hydrochloric acid, it yields a *hydrochloride*, $C_{22}H_{18}N_4,2HCl$, which is readily decomposed by water. The *nitrate* is a white powder which melts at 122°, with rapid evolution of gas. Sodium nitrite and hydrochloric acid have no action on the dihydrazidine.

Naphthenylbenzenylhydrazidine, $NH_2\cdot CPh{:}N\cdot N{:}C(C_{10}H_7)\cdot NH_2$, is obtained by the addition of free benzimido-ether to an alcoholic solution of naphthenylhydrazidine. The base is sparingly soluble in alcohol, cold acetone, or mineral acids, with the latter of which it forms salts. When heated, it decomposes and then melts at the same temperature as the triazole. 2 : 5-*Naphthylphenyltriazole*, which is most readily obtained by heating the preceding compound with glacial acetic acid, crystallises from alcohol in colourless prisms melting at 217°, and yields a white precipitate with silver nitrate. β-*Naphthenylparatolenylhydrazidine* melts at 202°, and the corresponding 2 : 5-*naphthylparatolyltriazole* at 190°. 2 : 5-*Dinaphthyltriazole*, obtained from the dihydrazidine on boiling it with acetic acid, melts at 222°; it yields a crystalline *silver* salt and an *acetyl* derivative melting at 187°. *Dinaphthyldihydrotetrazine* crystallises in thin, orange-coloured needles which are readily oxidised to the tetrazine. It has the same melting point as the tetrazine, and is sparingly soluble in alcohol. The *diacetyl* derivative, $C_{22}H_{14}N_4Ac_2$, crystallises in colourless prisms melting at 210°. *Dinaphthyltetrazine* crystallises in broad, flat, red needles melting at 246°, and sparingly soluble in benzene, readily in acetone or ethylic acetate. When boiled for 5—6 hours with aqueous potassium hydroxide, it yields *naphthoyl*-β-*naphthylidenehydrazide*, $C_{10}H_7\cdot CH{:}N\cdot N{:}C(OH)\cdot C_{10}H_7$.

2 : 5-*Dinaphthyldihydrotriazole* is obtained in a crystalline form when aqueous potassium hydroxide is added to an alcoholic solution of naphthenylhydrazidine and the mixture is allowed to stand for 6—8 weeks. It forms large, yellow plates, which are practically insoluble in the usual solvents with the exception of boiling glacial acetic acid. It melts and decomposes at 240°, yields a *diacetyl* derivative, $C_{22}H_{15}N_3Ac_2$, melting at 138°, and when heated at 150—160° with glacial acetic acid yields β-naphthoic acid and β-*naphthalazine*, $C_{10}H_7\cdot CH{:}N\cdot N{:}CH\cdot C_{10}H_7$, melting at 162°.

[With GÖBEL.]—No monhydrazidine can be obtained by the action of hydrazine on phenylacetimido-ether, $CH_2Ph\cdot C(OEt){:}NH$, the chief product being *diphenylacetohydrazidine*,

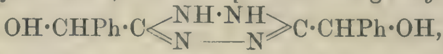
$$NH_2\cdot C(CH_2Ph){:}N\cdot N{:}C(CH_2Ph)\cdot NH_2,$$

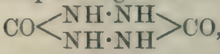
which crystallises from alcohol in yellowish plates melting at 153°. The *hydrochloride*, $C_{16}H_{18}N_4,HCl$, and *nitrate*, $C_{16}H_{18}N_4,HNO_3$, are described. 2 : 5-*Dibenzyltriazole*, obtained by boiling the above dihydrazidine for a short time with glacial acetic acid, crystallises in plates melting at 147°, and yields a *silver* salt decomposing at 170°.

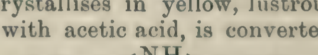
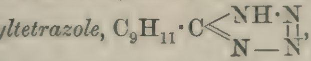
Dibenzyldihydrotetrazine crystallises from alcohol in reddish needles, and, when freshly prepared, melts at 158—160°, but after it has been kept for some time, it melts at a much lower temperature, owing to partial conversion into the tetrazine. When warmed with hydrochloric acid, the dihydrotetrazine is readily transformed into *dibenzylisodihydrotetrazine* melting at 162°; the latter is, however, always accompanied by a certain quantity of the hydrazide of phenylacetic acid. The *hydrochloride* and *nitrate*, $C_{16}H_{16}N_4,HNO_3$, of the isodihydrotetrazole and also a *diacetyl* derivative, melting at 93°, are described.

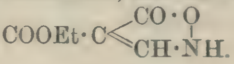
Diphenylacetohydrazide, $CH_2Ph\cdot CO\cdot NH\cdot NH\cdot CO\cdot CH_2Ph$, crystallises in needles melting at 231°.

Dibenzyltetrazine, which crystallises from dilute alcohol in long, flat prisms melting at 74°, is readily soluble in the usual organic solvents with the exception of light petroleum.

The imido-ether, $OH\cdot CHPh\cdot C(OEt)\colon NH$, obtained from mandelonitrile, when treated with hydrazine, yields neither a monhydrazidine nor a dihydrazidine, the chief product being *dihydroxydibenzyldihydrotetrazine*,  $OH\cdot CHPh\cdot C\Big<{NH\cdot NH \atop N\text{———}N}\Big>C\cdot CHPh\cdot OH$, which crystallises in yellowish needles melting at 193°. It yields a *tetracetyl* derivative melting at 203°. J. J. S.

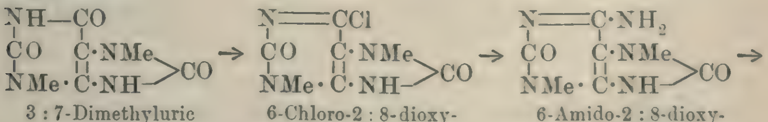
Action of Hydrazodicarbonamide on Hydrazine Sulphate. By ATTILIO PURGOTTI (*Gazzetta*, 1897, **27**, ii, 60—67).—On heating a mixture of hydrazine sulphate and hydrazodicarbonamide in an oil bath at 210—215°, ammonia and hydrogen sulphide are evolved, and on extracting with water, filtering and evaporating the solution, *paraurazine* or *paradiketohexahydrotetrazine*,  $CO\Big<{NH\cdot NH \atop NH\cdot NH}\Big>CO$, separates in small, colourless, brilliant, monosymmetric crystals melting and decomposing at 266—267° [$a:b:c = 1\cdot159:1:?$; $\beta = 87°\ 55'$]. Paraurazine has the normal molecular weight in boiling aqueous solution, and reduces ammoniacal silver nitrate in the cold, but is stable towards Fehling's solution; it behaves as a monobasic acid, giving a white *silver* salt, $C_2O_2N_4H_3Ag$. W. J. P.

Action of Hydrazine on Cumenylimido-ether. By JAMES COLMAN (*Ber.*, 1897, **30**, 2010—2011).—When the hydrochloride of cumenylimido-ether is treated with potassium carbonate and an alkaline solution of hydrazine sulphate, a precipitate is formed on standing which contains two compounds. Of these, *dicumenylhydrazidine*, $NH_2\cdot C(C_9H_{11})\colon N\cdot N\colon C(C_9H_{11})\cdot NH_2$, is insoluble in acetone but soluble in alcohol. It crystallises in yellow, lustrous plates, melts at 193°, and when boiled with acetic acid, is converted into 2 : 5-*diparaisopropylphenyltriazole*,  $C_9H_{11}\cdot C\Big<{NH \atop N\cdot N}\Big>C\cdot C_9H_{11}$, which crystallises in thin, colourless plates, and melts at 210°. The second compound is the corresponding *hydrazo*-derivative, which has not been obtained pure, since it oxidises in the air, forming *diparaisopropylphenyltetrazine*, $C_9H_{11}\cdot C\Big<{N\colon N \atop N\cdot N}\Big>C\cdot C_9H_{11}$, which crystallises in deep red plates melting at 156—157°. The filtrate from these two compounds contains *cumenylhydrazidine*, $C_9H_{11}\cdot C(NH_2)\colon N\cdot NH_2$, which has not itself been isolated, but is converted by sodium nitrite into *paraisopropylphenyltetrazole*,  $C_9H_{11}\cdot C{<}\begin{matrix}NH\cdot N\\ \,\,\,\,\,\,\,\,\,\,\,\,\,\, \| \\ N - N\end{matrix}$, which crystallises in long needles or broad plates melting at 189°. The *ammonium* and *barium* salts are both crystalline. The *methyl* derivative crystallises from alcohol in colourless plates melting at 120—122°. A. H.

Action of Hydroxylamine on Ethylic Dicarboxyglutaconate. By SIEGFRIED RUHEMANN (*Ber.*, 1897, **30**, 2031—2032. Compare Abstr., 1897, i, 445).—The researches of Claisen (this vol., i, 493), Uhlenhuth (*ibid.*, i, 444), and Rabe (*ibid.*, i, 568), show that the product formed by the action of hydroxylamine on ethylic dicarboxyglutaconate is identical with that formed by the action of hydroxylamine on ethylic ethoxymethylenemalonate, and has the constitution of ethylic isoxazolonecarboxylate,  $COOEt\cdot C{<}\begin{matrix}CO\cdot O\\ \,\,\,\,\,\,\,\, | \\ CH\cdot NH\end{matrix}$. A. H.

Action of the Electric Current on some Alkaloids. By HERBERT POMMEREHNE (*Arch. Pharm.*, 1897, **235**, 364—368).—Caffeine when decomposed by the electric current yields amalic acid, formic acid, ammonia, and methylamine, whilst morphine, when submitted to the same treatment, gives rise to oxydimorphine, and quinine to thalleioquinine. J. F. T.

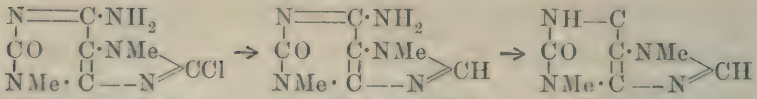
Synthesis of Theobromine. By EMIL FISCHER (*Ber.*, 1897, **30**, 1839—1845).—3 : 7-Dimethyluric (γ-dimethyluric) acid has now been prepared synthetically (this vol., i, 268), and from it dimethyldioxychloropurine (chlorodioxydimethylpurine) can be obtained by the combined action of phosphorus pentachloride and oxychloride (Abstr., 1896, i, 13). The product of the latter reaction, when heated at 130° with four times its weight of aqueous ammonia (saturated at 0°) for 3 hours in a sealed tube, yields 6-*amido*-2 : 8-*dioxy*-3 : 7-*dimethylpurine*; when heated, this decomposes without melting. It forms salts with acids, and also yields sodium, potassium, and ammonium derivatives, the latter of which is decomposed on the water bath. When heated for 4 hours at 170° with ten times its weight of phosphorus oxychloride, it yields 8-*chloro*-6-*amido*-2-*oxy*-3 : 7-*dimethylpurine*, which crystallises with $3H_2O$, decomposes without melting, when heated, and has basic properties. This substance, when warmed with four times its weight of hydriodic acid of sp. gr. 1·96 and a little powdered phosphonium iodide, is reduced to 6-*amido*-2-*oxy*-3 : 7-*dimethylpurine*, which crystallises with $3H_2O$, decomposes when heated, and is still unmelted at 380°, and has basic properties; when dissolved in dilute sulphuric acid, and heated with sodium nitrite, it yields theobromine, to which the formula given below must be assigned in consequence.



3 : 7-Dimethyluric acid.

6-Chloro-2 : 8-dioxy-3 : 7-dimethylpurine.

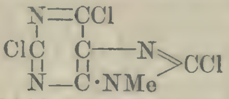
6-Amido-2 : 8-dioxy-3 : 7-dimethylpurine.



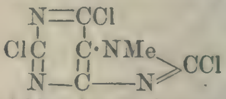
8-Chloro-6-amido-2-oxy-3 : 7-dimethylpurine. 6-Amido-2-oxy-3 : 7-dimethylpurine. Theobromine.

C. F. B.

The Two Methyltrichloropurines. By Emil Fischer (*Ber.*, 1897, 30, 1846—1859; for the nomenclature compare this vol., i, 268, where the 8 and 9 should be interchanged).—Both 9- and 7- (formerly α- and β-; Abstr., 1884, 996, and 1896, i, 13) methyltrichloropurine react



Trichloro-9-methylpurine (α).



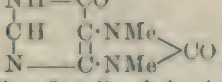
Trichloro-7-methylpurine (β).

with alkalis, the 9 compound more easily, and yield the same products as when they react with hydrochloric acid, one Cl being exchanged for OH, and an 8-oxy compound formed. With alcoholic potash, two chlorine atoms are attacked, and diethoxy-compounds are formed; the second chlorine atom attacked is certainly in the 6-position in the case of the 7-methyl compound, and presumably so in the case of the other. These ethoxy-compounds can be hydrolysed to the oxy-compounds by heating with strong hydrochloric acid on the water bath, whilst with hydriodic acid and phosphonium iodide, the remaining chlorine atom can be replaced by hydrogen.

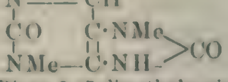
Aqueous potash acts on trichloro-7-methylpurine at the ordinary temperature, but more rapidly at 100°, yielding 2 : 6-dichloro-8-oxy-7-methylpurine. Alcoholic potash at 3° forms 2 : 6-*dichloro-8-ethoxy-7-methylpurine*, melting at 185—186° (corr.); at 35—40°, it forms 2-*chloro-6 : 8-diethoxy-7-methylpurine*, which melts at 194—195° (corr.), yields a *chloromethyloxyethoxypurine* melting at 270—271° (corr.), when hydrolysed with hydriodic acid, and 6 : 8-*dioxy-7-methylpurine* when reduced with hydriodic acid and phosphonium iodide; the last named substance turns brown at about 400°, or melts if heated rapidly, and has both acid and basic properties.

Aqueous potash acts on trichloro-9-methylpurine only at the boiling temperature, and even then 2 : 6-dichloro-8-oxy-9-methylpurine is not the only product. Alcoholic potash at 5° forms 2 : 6-*dichloro-8-ethoxy-9-methylpurine*, which melts at 154° (corr.); at the boiling temperature it forms *chlorodiethoxy-9-methylpurine* (presumably 2-chloro-6 : 8-diethoxy-), which melts at 149—150° (corr.), and when hydrolysed with hydrochloric acid yields a product melting at 264°.

The compounds formerly known as α- and β-dimethyldioxypurine (*loc. cit.*) can now be identified respectively as 6 : 8-dioxy-7 : 9-dimethylpurine and 2 : 8-dioxy-3 : 7-dimethylpurine. For the β-compound is prepared by



6 : 8-Dioxy-7 : 9-dimethylpurine (α).



2 : 8-Dioxy-3 : 7-dimethylpurine (β).

reducing the dimethyldioxychloropurine obtained from 3 : 7-dimethyluric acid (compare synthesis of theobromine, this vol., i, 641). And the α-isomeride is known to be an 8-oxy compound. These compounds can be methylated by heating them with aqueous potash and methylic iodide in a sealed tube at 100°. They yield respectively 6 : 8-*dioxy-1 : 7 : 9-trimethylpurine*, which melts at 235—236° (corr.), and can also be obtained by methylating 6 : 8-dioxy-7-methylpurine ; and 2 : 8-*dioxy-3 : 7 : 9-trimethylpurine*, which melts at 254° (corr.). Both of these substances have basic properties ; the *aurochloride* of the first contains water of crystallisation (?, $2H_2O$), that of the second is anhydrous ; both differ from caffeine in that they do not give the murexide test after treatment with chlorine water.

[With Friedrich Jacobi.]—When an alcoholic solution of 7-methyltrichloropurine is saturated with ammonia, 2 : 6-*dichloro-8-amido-7-methylpurine* is formed. This decomposes at a high temperature without melting ; it has basic properties, and dissolves also in alkalis ; when reduced with hydriodic acid and phosphonium iodide on the water bath, it forms 8-*amido-7-methylpurine*, which decomposes without melting completely, and is basic in character ; when hydrolysed with strong hydrochloric acid in a sealed tube at 120—130°, it yields 8-*amido-2 : 6-dioxy-7-methylpurine*, which has both basic and acid properties (the *sodium* salt, $C_6H_6N_5O_2Na + 2H_2O$, was analysed), and is oxidised by warm nitric acid to alloxan, in consequence of which it gives the murexide test. C. F. B.

Ammonium Bases of the Morphine Group. By Eduard Vongerichten (*Annalen*, 1897, **297**, 204—220.)—*Bromodiacetylmorphine*, $C_{21}H_{22}BrNO_5$, is obtained by treating diacetylmorphine suspended in water with an aqueous solution of the calculated amount of bromine ; the perbromide at first precipitated gradually disappears, and bromodiacetylmorphine separates on adding sodium carbonate to the reddish-brown liquid. It crystallises in colourless prisms, and melts at 208°.

Bromomorphine, $C_{17}H_{18}BrNO_3$, produced by the action of alcoholic sodium methoxide on the foregoing substance, crystallises from alcohol in small prisms ; when precipitated by alkalis from aqueous solutions of its salts, bromomorphine forms a crystalline powder containing $\frac{1}{2}H_2O$, and softens at 120°. The substance does not dissolve in the calculated amount of sodium hydroxide, and, unlike morphine, requires considerable excess of the alkali for dissolution ; when treated in alcoholic solution with sodium ethoxide and methylic iodide, one-half remains unchanged, a very small proportion undergoing conversion into bromocodeine, the remainder yielding a mixture of methiodides. A solution of bromomorphine in dilute nitric acid does not yield a precipitate when heated with silver nitrate at 90° ; on adding a few drops of the concentrated acid, however, silver bromide is precipitated after a short interval, nitromorphine being probably formed. Oxidising agents which convert morphine into pseudomorphine have no effect on bromomorphine under the same condition. The *hydrochloride* crystallises from water in white needles containing $3H_2O$, and is less readily soluble in water than morphine hydrochloride; the *methiodide* crystallises from water in colourless prisms containing $1H_2O$, and melts and decomposes at 252°. The *methoxide* forms slender needles, and when treated with methylic alcohol and methylic iodide yields the *methiodide* of bromocodeine, which contains $1H_2O$; it crystallises in stellar aggregates of prisms, and melts at 242—244°.

Bromomethylmorphimethine, $C_{19}H_{22}BrNO_3$, is obtained by treating bromocodeine methiodide with alkalis, and crystallises from methylic alcohol in white leaflets; it melts at 132°, and remains turbid until 180°, when it becomes brownish, but if heated to 170—175°, and allowed to cool, it solidifies in white needles at 150—145°, and in this form melts at 182—184°. The solution in concentrated sulphuric acid is brownish-black, and becomes pale bluish-green after a time. The *platinochloride* contains $4H_2O$. *Acetoxymethoxybromophenanthrene*, $C_{17}H_{13}BrO_3$, is produced on heating bromomethylmorphimethine with acetic anhydride for several days in a reflux apparatus; it crystallises from methylic alcohol in stellate groups of needles, and melts at 166°.

Chlorocodide *methiodide*, $C_{18}H_{20}ClNO_2,MeI$, is prepared by dissolving chlorocodide in cold methylic iodide, separation of iodine occurring when the substances are heated. The *methohydroxide* is strongly alkaline, and gives no precipitate with silver nitrate; on boiling the aqueous solution, however, the liquid becomes neutral, and the addition of silver nitrate then produces a precipitate of silver chloride.

Bromodiacetylmorphine *methiodide* crystallises in stellate groups of needles containing $1\frac{1}{2}H_2O$; it softens at 185°, and melts at 200°, evolving gas. The *methohydroxide* is very unstable, and in aqueous solution becomes converted spontaneously into the acetate of bromacetylmorphine methohydroxide. When potassium iodide is added to the aqueous solution of this substance and the liquid concentrated, the *methiodide* of bromacetylmorphine is obtained in wedge-shaped plates containing $2H_2O$; it melts indefinitely and evolves gas at 215—220°. The *methohydroxide* of bromacetylmorphine is syrupy, and yields bromacetylcodeine methiodide when heated with methylic iodide and methylic alcohol.

Bromacetylcodeine *methohydroxide* is obtained from the methiodide, and yields the acetate of bromomethylmorphimethine when the aqueous solution is concentrated. Bromocodeine *methochloride* crystallises in silky needles, and contains $2\frac{1}{2}H_2O$; when heated with acetic anhydride on the water bath, it yields bromacetylcodeine methochloride, and on heating the aqueous solution of the corresponding methohydroxide, it becomes neutral, and contains bromomethylmorphimethine.

Acetylcodeine *methiodide* forms long, colourless needles melting and evolving gas at 250—252°; the *methohydroxide*, when heated in aqueous solution, is converted into the acetate of codeine methohydroxide.

M. O. F.

Action of Bromacetophenone on Strychnine. By Hans Rumpel (*Arch. Pharm.*, 1897, **235**, 398—400).—If a solution of strychnine is added to a chloroform solution of bromacetophenone, a crystalline substance begins to separate immediately; this is *strychnine* *acetophenone bromide*, $C_{21}H_{22}N_2O_2,C_6H_5{\cdot}CO{\cdot}CH_2Br + H_{20}$, which crystallises in colourless needles melting at 245—250° ; the corresponding *chloride*, prepared by treating the bromide with silver chloride, forms small nodules melting at 232—233°. J. F. T.

Alkaloids contained in the Seeds of Blue and White Lupins. By L. Sherman Davis (*Arch. Pharm.*, 1897, **235**, 199—240). See this vol., i, 174. E. W. W.

Alkaloids contained in the Seeds of Lupins. By Ernst Schmidt (*Arch. Pharm.*, 1897, **235**, 192—198).—A short *resumé* of previous investigations is given. In the seeds of *Lupinus luteus* and of *L. niger*, the author found lupinine, $C_{21}H_{40}N_2O_2$, and lupinidine, $C_8H_{15}N$. The molecular weight of the latter was determined by Raoult's method. The seeds of *L. perennis* contain dextrolupanine and another alkaloid not yet identified. E. W. W.

Lupinine and Lupinidine from Yellow Lupins. By L. Berend (Marburg) (*Arch. Pharm.*, 1897, **235**, 262—289).—The alkaloids were extracted from the seeds of *Lupinus luteus* by means of alcoholic hydrochloric acid, the extract being made alkaline, extracted with ether, and the mixed alkaloids separated as mercurochlorides. *Lupinine*, $C_{21}H_{40}N_2O_2$, which crystallises from light petroleum in colourless needles or rhombic plates melting at 67—68°, is easily soluble in ether and chloroform ; its specific rotation is $[\alpha]_D = -20$ in a 0·95 per cent. solution. The *platinochloride* forms yellow crystals melting at 163—164°, and the *aurochloride* glistening, transparent needles melting at 196—197° ; the *hydrochloride*, in a 2 per cent. solution, gives $[\alpha]_D = -14°$. Bromine does not give rise to any definite bromo-derivative, whilst phosphoric anhydride and hydrochloric acid produce anhydrolupinine and *dianhydrolupinine*, $C_{21}H_{36}N$, the latter forming a dark red *platinochloride* ; no trace of oxylupinine could be observed. On treatment with acetic anhydride, lupinine yields a *diacetyl* compound, the *aurochloride* of which melts at 120°. The presence of two hydroxyl groups in lupinine is shown by the formation of a well-defined although unstable *dichloro*-derivative, when it is treated with phosphorus pentachloride or phosphorus oxychloride ; the *aurochloride* of this compound consists of stellate groups of needles. Like lupinine, dianhydrolupinine combines with 2 mols. of methylic iodide ; the corresponding *aurochloride* melts at 180°.

Lupinidine, $C_8H_{15}N$, is a yellowish-brown oil having an agreeable ethereal odour when pure ; the *sulphate* melts and decomposes at about 180° ; the *platinochloride* crystallises with $2H_2O$ and melts at 227°, the *aurochloride* forms slender needles melting at 189°, and the *mercurochloride* is a white, crystalline powder which decomposes at 200°. The *hydriodide*, $C_8H_5N,HI + \frac{1}{2}H_2O$, which is most conveniently obtained by treating a solution of the hydrochloride with potassium iodide, consists of glistening plates ; the *basic hydriodide*, $(C_8H_5N)_2,HI$, on the other hand, prepared by treating the alkaloid with hydriodic acid, or by the action of ethylic iodide on the hydrochloride, consists of transparent, rhombic prisms melting at 230°. J. F. T.

The Alkaloids of the Black Lupin. By K. GERHARD (*Arch. Pharm.*, 1897, **235**, 342—355).—A quantitative estimation of the alkaloids contained in the different varieties of lupin seeds gave the following results.

	Estimated as lupanine, $C_{15}H_{24}N_2O$.	as lupinine, $C_{21}H_{40}N_2O_2$.
Yellow	0·4493 per cent.	0·6378 per cent.
Blue	0·7249 ,,	—
White	1·1115 ,,	—
Perennial	1·1829 ,,	—
Black	0·6100 ,,	0·8659 ,,

The alkaloids extracted from the black lupins are the same as those derived from the yellow varieties, namely, lupinine and lupinidine. Various salts of these alkaloids obtained from the different varieties of lupin are described in detail (compare Berend, preceding abstract).

J. F. T.

Alkaloids of the Perennial Lupin (Lupinus polyphyllus) (*Arch. Pharm.*, 1897, **235**, 355—363), **and of other Species of Lupin** (pp. 363—364). By K. GERHARD.—The alkaloid derived from the seeds of *Lupinus polyphyllus* is identical with the dextrolupanine, $C_{15}H_{24}N_2O$, obtained from the seeds of the blue lupin by Davis (this vol., i, 174). The hydrochloride, hydriodide, platinochloride, aurochloride, and thiocyanate of the base are described.

The seeds of *L. affinis*, *L. albococcineus*, *L. Cruikshanksi*, *L. Moritzianus*, *L. mutabilis*, and *L. pubescens* were also examined; they all contained alkaloids, but they were not extracted in quantity sufficient to characterise them.

J. F. T.

Alkaloids of the Lupinus Albus. By ARTURO SOLDAINI (*Arch. Pharm.*, 1897, **235**, 368—374).—The main facts have already appeared (compare Abstr., 1896, i, 193).

J. F. T.

Cytisine. By J. LAMMERS (*Arch. Pharm.*, 1897, **235**, 374—397).—The alkaloid used for these investigations was obtained from the laburnum seed. *Dibromocytisine*, obtained from its hydrobromide, crystallises from absolute alcohol in fine white crystals melting at 65—73°, and yields the alkaloid on reduction, both in acid and alkaline solution (see baptitoxine, this vol., i, 627). *Bromocytisine*, which is formed on reducing the hydrobromide of the dibromo-derivative with zinc and acetic acid, is a brownish-yellow oil; the *hydrobromide*, $2(C_{11}H_{13}BrN_2O,HBr) + 3H_2O$, consists of colourless prisms; the *hydrochloride*, which crystallises with $2H_2O$ of fine, white prisms, the *platinochloride* $(C_{11}H_{13}BrN_2O)_2,H_2PtCl_6 + H_2O$ of yellow needles, the *aurochloride* of orange-red crystals melting at 217°, the *tartrate* of colourless plates, the *nitrate*, crystallising with $1H_2O$, in broad prisms. The *methiodide* crystallises in anhydrous, white needles, and the *methochloride* in fine, white crystals; the *aurochloride* of monobromomethylcytisine forms golden-yellow crystals, and the *platinochloride* brownish-red plates. *Methylcytisine*, $C_{11}H_{13}N_2O{\cdot}CH_3$, obtained from the methiodide by treating it with potassium hydroxide, yields *dibromomethylcytisine hydrobromide* on bromination; this separates from its warm, aqueous solution in slender needles melting at 197—198°. The corresponding *hydrochloride* forms fine, white crystals, and the *platinochloride* yellow needles stable at 250°.

Dibromocytisine methiodide, $C_{11}H_{11}Br_2N_2O\cdot CH_3,HI$, crystallises in white needles soluble in water, and on methylation gave rise to a compound identical with that prepared by the bromination of methylcytisine; the bromine atom cannot therefore have replaced the hydrogen in the imido-group of the alkaloid.

Dichlorocytisine is prepared by the chlorination of cytisine; its *hydrobromide*, $2(C_{11}H_{12}Cl_2N_2O,HBr) + H_2O$, crystallises in white needles, the *hydrochloride* in fine, anhydrous white needles, the *platinochloride*, in orange-yellow, soluble needles, and the *aurochloride* in red needles.

J. F. T.

Carpaine. By J. J. L. VAN RIJN (*Arch. Pharm.*, 1897, **235**, 332—342).—This is a preliminary paper, dealing with carpaine, the alkaloid, $C_{14}H_2NO_2$, extracted from *Carica papaya*, L. On methylation, it yields *methylcarpaine* crystallising from dilute alcohol in small, colourless prisms melting at 71°, benzoylation of nitrosocarpaine yields a colourless crystalline substance melting at 100°, and containing the nitroso-group unchanged; the alkaloid on oxidation with potassium permanganate in acid solution, gives rise to a variety of compounds which are still under investigation. The paper concludes with a crystallographic description of carpaine and its principal salts. J. F. T.

Biliverdic Acid, a Product of the Hydrolysis of the Colouring-matter of Bile. By WILLIAM KÜSTER (*Ber.*, 1897, **30**, 1831—1835).—Bilirubin, $C_{16}H_{18}N_2O_4$, was prepared from gall-stones by Maly's method. (This Journal, 1875, 651.) It was dissolved (1 mol.) in acetic acid, and treated gradually with a concentrated aqueous solution of sodium dichromate (equivalent to 6 atoms oxygen); only 3 atoms of oxygen reacted at 20°, the rest at 100°. Sulphuric acid equivalent to the sodium present was added, the acetic acid evaporated, and the residual liquid extracted with ether; from this extract, yellowish crystals of a substance, $C_8H_9NO_4$, were obtained. To this the name of *biliverdic acid* is given; it behaves like a monobasic acid with N 5 ammonia, but a neutral solution of the ammonium salt gives, with silver nitrate, a precipitate containing 2 atoms of silver in the molecule; it has, moreover, the character of an unsaturated compound, for it decolorises permanganate instantaneously in the cold; it evolves no ammonia when it is boiled with alkalis, neither has it any basic properties. The author inclines to the opinion that the nitrogen is present as a cyanogen group, in which case the substance might be nearly related to hæmatic acid, $C_8H_8O_5$, the product of the oxidation of hæmatoporphyrin (this vol., i, 232). C. F. B.

Deoxycholic acid. By ERNST VAHLEN (*Zeit. physiol. Chem.* 1897, **23**, 99—108).—Some time since, the author described (Abstr., 1896, i, 453) a substance isolated from putrefied ox-bile, which he believed to be different from choleic acid and identical with the deoxycholic acid described by Mylius (Abstr., 1886, 481). By fractionally precipitating the bile with barium chloride, a salt is obtained yielding a free acid which crystallises from glacial acetic acid in delicate prisms, melts at 140—145°, and on analysis gives numbers agreeing well with those required for deoxycholic acid.

As it is difficult to separate this acid from admixed choleic acid, experiments were made on the reduction of pure cholic acid, to ascertain if by this means a similar substance could be obtained.

When cholic acid is treated with zinc dust in acetic acid solution, an acid is obtained which crystallises from glacial acetic acid and melts at 140—145°. The barium salt crystallises in microscopic needles, is unlike the barium salt of choleic acid, and is apparently identical with the salt obtained from fermented ox-bile.

The acid melting at 140—145° is also obtained by reducing choleic acid in alkaline solution, and the author proposes to further investigate the exact composition of this substance. A. W. C.

Bromalbumin and its Behaviour towards Microbes. By Oscar Loew and S. Takabayashi (*Bull. Coll. Agric. Imp. Univ. Tokyo*, 1897, **3**, 237—240).—Bromalbumin (Abstr., 1885, 823) is now prepared by mixing equal weights of albumin and bromine, which must be cooled during the operation, and then heating the mixture at 60° for two days. The product is washed successively with water, sulphurous acid, dilute sodium carbonate, 50 per cent. alcohol, and absolute alcohol. The substance, dried at 100°, contains 10·64—11·0 per cent. of bromine.

Experiments with 1 per cent. solutions of bromalbumin, with and without peptone and cane-sugar respectively, showed that the compound is not favourable for the development of microbes (putrefaction microbes and bacilli of anthrax) in absence of air, even in presence of sugar, but does not prevent development in presence of peptone.

N. H. J. M.

Iodo-Derivatives of Proteids (Casein). By A. Liebrecht (*Ber.*, 1897, **30**, 1824—1826).—*Periodocasein* is obtained as a yellow powder by warming an intimate mixture of casein with a quarter of its weight of iodine on the water bath, and removing the excess of iodine by extraction with ether, or by boiling casein with 70 per cent. alcohol and iodine; it contains 17·8 per cent. of iodine, and dissolves in hot, dilute alcohol. When it is treated with an alkaline thiosulphate, and then washed with water, alcohol, and ether, it yields *iodocasein*, a white substance which contains 5·7 per cent. of iodine, is insoluble in the commoner solvents, and, like casein, has acid properties. If it is heated with about 20 times its weight of 10 per cent. sulphuric acid for 2 hours on the water bath, it yields *caseoiodin*, a white powder which contains about 8·7 (8·5—9·3) per cent. of iodine, has acid properties, gives the biuret reaction, and resembles iodothyrin in its physiological action. C. F. B.

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